RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XII NUMBER 4

October, 1939

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

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of the American Chemical Society,
1500 Greenmount Avenue,
Baltimore, Md.

Editor ..... C. C. DAVIS
Advertising Manager ..... S. G. BYAM
Secretary ..... H. I. CRAMER
Treasurer ..... C. W. CHRISTENSEN

Vol. XII October, 1939 No. 4

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry upon payment of the dues ($2.50) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, extra postage must be added at the rate of $.20 per year for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

Articles, including translations and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman...E. B. CURTIS, R. T. Vanderbilt Co., 230 Park Ave., New York, N. Y.
Vice-Chairman....R. H. GERKE, General Laboratories, United States Rubber Co., Passaic, N. J.
Secretary.....H. I. CRAMER, University of Akron, Akron, Ohio
Treasurer.....C. W. CHRISTENSEN, Monsanto Chemical Co., Akron, Ohio
Sergeant-at-Arms.....C. P. HALL
Editor of *Rubber Chemistry and Technology*.....C. C. DAVIS
Advertising Manager of *Rubber Chemistry and Technology*.....S. G. BYAM
Directors.....G. K. HINSHAW, E. B. BABCOCK, W. F. BUSSE, J. H. INGMANSON, A. H. NELLEN

THE FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY, BOSTON, MASSACHUSETTS, SEPTEMBER 11-15, 1937

The Division opened its program by participating in two symposia arranged by other divisions:

1. Plastics and Resins from Hydrocarbons. Divisions of Petroleum and Paint and Varnish Chemistry, September 11.
2. X-Ray Studies of Substances of High Molecular Weight. Divisions of Physical and Inorganic, Colloid and Organic Chemistry, September 12.

Members of the Division of Rubber Chemistry gave papers at both symposia.

The American Chemical Society held its general meeting, under the aupices of the Division of Rubber Chemistry, in Symphony Hall, Wednesday afternoon, September 13. This meeting began the exercises devoted to the commemoration of the discovery of vulcanization of rubber by Charles Goodyear. George K. Hinshaw, Chairman of the Division of Rubber Chemistry reviewed the history of the Division, organized in 1919, and of its predecessor, the India Rubber Section of the American Chemical Society, founded in 1909. He paid tribute to Charles Goodyear as the man who, after years of sacrifice and persevering labor, made the discovery that marked the birth of the modern rubber industry. He pointed out the fitness of devoting the program of the general meeting to a review of the contributions of this early inventor and his contemporary in England, Thomas Hancock. It was announced that the Board of Directors of the American Chemical Society had voted to sponsor the nomination of Charles Goodyear to the Hall of Fame Electors for a place in the Hall of Fame. The following papers were then presented:

1. What is Vulcanization?—E. B. Babcock.
2. The Work of Thomas Hancock.—A. A. Glidden.
3. The Work of Charles Goodyear.—R. W. Lunn, Birmingham, England (read by W. B. Wiegand).
4. The Rubber Industry Since 1839.—W. A. Gibbons.

The Centennial Celebration was continued by a subscription dinner at the Copley-Plaza Hotel, at which approximately 965 members and guests enjoyed

a sumptuous banquet, with J. M. Bierer, Chairman of the Goodyear Centennial Committee, as toastmaster. He reviewed the history of the rubber industry and introduced three guest speakers:

1. Paul W. Litchfield, President of the Goodyear Tire and Rubber Co.,—"Rubber's Position in Modern Civilization."
2. Karl T. Compton, President of Massachusetts Institute of Technology,—"Looking Forward in Research."
3. James B. Conant, President of Harvard University,—"Lessons from the Past."

Souvenirs were distributed at the banquet, among which were a volume combining Charles Goodyear's "Gum Elastic" and Thomas Hancock's "Personal Narrative," and a booklet, beautifully prepared, containing the addresses given at the dinner and at the general meeting. The Division is indebted to the following companies for funds to purchase these souvenirs:

American Cyanamid & Chemical Corporation
American Zinc Sales Company
H. A. Astlett & Company
Robert Badenhop Corporation
The Barrett Company
Bibb Manufacturing Company
Binney & Smith Company
Boston Woven Hose & Rubber Company
Godfrey L. Cabot, Inc.
Callaway Mills
Cleveland Liner & Mfg. Company
Columbian Carbon Company
Converse Rubber Company
The Dill Manufacturing Company
E. I. Du Pont de Nemours & Company Inc.
Eagle-Picher Lead Company
Emerson Apparatus Company
Farrel-Birmingham Company, Inc.
Firestone Tire & Rubber Company
The Fisk Rubber Corporation
The Flintkote Company
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The B. F. Goodrich Company
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The Holliston Mills, Inc.
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J. H. Lane & Company
Littlejohn & Company, Inc.
Midwest Rubber Reclaiming Company
Monsanto Chemical Company (Rubber Service Laboratories Division)
Moore & Munger
H. Muehlstein & Company, Inc.
National Erie Corporation
Naugatuck Chemical
New Jersey Zinc Company
Pequanoc Rubber Company
Rare Metal Products Company
John Robertson Company, Inc.
A. Schrader's Son
A. Schulman, Inc.
Henry L. Scott Company, Inc.
The Seamless Rubber Company, Inc.
Simplex Wire & Cable Company
Somerset Rubber Reclaiming Works
Spadone Machine Company, Inc.
Stamford Rubber Supply Company
Stauffer Chemical Company
J. P. Stevens & Company, Inc.
St. Joseph Lead Company
C. J. Tagliabue Mfg. Company
Thiokol Corporation
Thompson, Weinman & Company, Inc.
Titanium Pigment Corporation
Turner Halsey Company
United Carbon Company, Inc.
United States Rubber Company
U. S. Rubber Reclaiming Company, Inc.
R. T. Vanderbilt Company, Inc.
Vansul, Inc.
Vultex Chemical Company
Wellington Sears Company, Inc.
C. K. Williams & Company
Charles T. Wilson Company, Inc.
Wishnick-Tumpeer, Inc.

Both of these affairs were arranged by a committee composed of J. M. Bierer, *Chairman*, C. R. Boggs, A. A. Somerville, W. B. Wiegand, G. K. Hinshaw and E. B. Curtis. The very successful programs represented two years of careful work and planning by this committee and several sub-committees.

The technical sessions of the Division were held in the Parker House, September 14-15, with 350-500 in attendance.

The first day and part of the next forenoon were devoted to a Symposium on Vulcanization, comprising the following papers:

1. The Vulcanization of Rubber. H. L. Fisher.
2. Physical Changes Induced by Vulcanization. W. W. Vogt.
3. Effect of Vulcanization on the Structure of Rubber—A Problem in Probabilities. W. F. Busse.
4. Some Relations Between Vulcanization and Reinforcement. C. R. Park.
5. The X-Ray Structure of Vulcanized Rubber. G. L. Clark.
6. Effect of Variability of Rubber on Vulcanization. Edgar Rhodes (Read by R. A. Crawford).
7. Methods for the Control of Vulcanization by the Individual Incorporation of Vulcanizing Agents. D. F. Twiss (Read by C. R. Park).
8. Theories of Acceleration. L. B. Sebrell.
9. The Vulcanization of Rubber from a Thermodynamic Viewpoint. Ira Williams.
10. The Mechanism of Oxidation of Vulcanized Rubber. A. R. Kemp, J. H. Ingmanson and G. S. Mueller.
11. Influence of Vulcanization on Oxidizability—Vulcanizing Agents Other Than Sulfur. Charles Dufraisse and J. Le Bras (Read by A. R. Kemp).
12. What is Optimum Cure? J. C. Walton.
13. Temperature Coefficient of Vulcanization. R. H. Gerke.
14. Effect of Reclaimed Rubber on Temperature Coefficient of Vulcanization. W. S. Coe.
15. Low Temperature Set as a Measure of State of Vulcanization. J. H. Fielding.
16. The Vulcanization of Latex. C. E. Bradley

The remainder of the second day was devoted to general papers:

1. The Rubberlike Properties of Polybutene. W. J. Sparks, I. E. Lightbown, L. B. Turner, P. K. Frolich and C. A. Klebsattel.
2. Catalytic Dehydrogenation of Monoölefins to Diolefins. A. V. Grosse, J. C. Morrell and J. M. Mavity.
3. Dielectric Constant of Rubber—Carbon Black Mixtures. C. M. Doede.
4. Practical Evaluation of Commercial Rubber Carbon Blacks by X-Ray Diffraction. G. L. Clark and H. D. Rhodes.
5. The Statistical Theory of the Elastic and Thermoelastic Properties of Rubber. E. Guth.
6. A New Method for Measurement of the Permeability of Rubber to Various Gases. A. S. Carpenter and D. F. Twiss (Read by S. D. Gehman).
7. The Dynamic Fatigue Life of Rubber. S. M. Cadwell, R. A. Merrill, C. M. Sloman and F. L. Yost.
8. The Analysis of Rubber for Antioxidants. L. H. Howland and E. J. Hart.
9. The Chloroform Extract of Reclaimed Rubber. H. F. Palmer and F. L. Kilbourne, Jr.

Chairman Hinshaw expressed the regret of the Division that the English and French authors who had submitted papers could not attend, and expressed the appreciation of the Division for their contributions.

R. H. Gerke reported progress made by the Crude Rubber Committee during the past six months. Tentative procedures for testing latex have been completed and will be published soon. The entire report will be published at a later date in *Rubber Chemistry and Technology*.

Chairman Hinshaw extended to J. M. Bierer his sincere personal thanks and

that of the Division for his excellent work as Chairman of the Goodyear Centennial Committee.

At the business meeting, the report of the Charles Goodyear Award Committee, headed by A. R. Kemp, was presented. The Executive Committee increased the honorarium from $150 to $200, and recommended that the award be in the form of a lectureship instead of a medal (the rules and regulations governing this award appear later).

Mr. Christensen discussed the provisions of the new by-laws, drawn up by a committee headed by himself, which had already been distributed in mimeographed form. It was voted unanimously to adopt the new by-laws. (These by-laws appear elsewhere in this issue).

The following technical and research organizations in foreign countries appointed official delegates to represent them at this historic meeting:

1. The National Research Council of Canada..... T. R. Griffith.
2. Institute of Chemistry of Great Britain and Ireland.. H. A. Tempany.
3. Research Association of British Rubber Manufacturers ..... R. W. Lunn.
4. London Advisory Committee for Rubber Research... Edgar Rhodes.
5. British Rubber Producers Research Association..... Edgar Rhodes.
6. Rubber Research Institute of Malaya..... J. H. Piddelsden.
7. Association Française des Ingenieurs du Caoutchouc.. Étienne de Meeus. Robert Thiollet.

However, because of the crisis in Europe, representatives of only (1), (6) and (7) attended. The Division was glad to welcome these men at its meetings. Mr. Griffith conveyed greetings from his organization and colleagues in Canada.

H. L. Trumbull, Chairman of the Nomenclature Committee, reported that his committee is studying first the problem of the nomenclature of synthetic products. This committee is coöperating with a committee of the American Society for Testing Materials working on the same problem. He invited members to submit suggestions and recommendations for consideration by the committee.

The report of the Nominating Committee was presented by S. M. Cadwell, Chairman. The following officers were elected for 1939-40:

Chairman	E. B. Curtis.
Vice-Chairman	R. H. Gerke.
Secretary	H. I. Cramer.
Treasurer	C. W. Christensen.
Sergeant-at-arms	C. P. Hall.
Directors	G. K. Hinshaw.
	E. B. Babcock.
	W. F. Busse.
	J. H. Ingmanson.
	A. H. Nellen.

Secretary's Report:

Total Membership to date, August 31, 1939		616
Members paid for 1939	475	
Associate Members paid for 1939	141	
New Members and Associate Members from March 31, 1939, to August 31, 1939 (included in above figure)		34
Regular Members	25	
Associate Members	9	
Subscriptions to *Rubber Chemistry and Technology*		198
Honorary Members and Exchange		25

H. I. CRAMER, *Secretary.*

NEW BY-LAWS OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

Be it resolved, by the vote of two-thirds of the Members present at the annual meeting of The Division of Rubber Chemistry of the American Chemical Society (hereinafter called "The Division"), held this 15th day of September 1939 in the City of Boston, State of Massachusetts, that:

1. These By-Laws of The Division are subject to the Constitution and By-Laws of the American Chemical Society and supersede all motions, rules and by-laws of any nature whatsoever previously enacted by The Division which are in conflict herewith.

2. CLASSES OF MEMBERSHIP. The membership of The Division shall comprise:

A. *Members.*—Any member of the American Chemical Society may become a Member of The Division on payment of the annual dues of two dollars and fifty cents ($2.50). Only Members shall have the right to vote and hold office. Each Member shall receive *Rubber Chemistry and Technology* without additional cost, except that Members living outside of the United States shall pay mailing charges as prescribed by the Treasurer.

B. *Associate Members.*—Any person may become an Associate Member on payment of annual dues of five dollars ($5.00). Associate Members are not members of the American Chemical Society and are entitled to none of its other privileges. They shall not be eligible to vote or hold office. Each Associate Member shall receive *Rubber Chemistry and Technology* without additional cost, except that Associate Members living outside of the United States shall pay mailing charges as prescribed by the Treasurer.

3. SUBSCRIPTIONS. Libraries and companies may subscribe to *Rubber Chemistry and Technology* at the rate of five dollars ($5.00) per year. Mailing charges shall be prescribed by the Treasurer for those libraries and companies outside of the United States.

Members of all classes shall be automatically dropped from the membership rolls and subscriptions shall be terminated unless dues and subscriptions, respectively, are paid in full by February 20 of each year.

4. OFFICERS. The Officers of The Division shall be the Chairman, Vice-Chairman, Secretary, Sergeant-at-Arms and Treasurer (although one person may hold the office of Secretary and Treasurer), whose duties shall be those ordinarily performed by such officials, and shall include the duties hereby delegated to the respective officials, and such duties as may from time to time be delegated to them.

The Executive Committee shall have the authority to fill any vacancy which may occur in any office, including Directors.

The Secretary shall arrange the program for each meeting. Not less than ninety (90) days prior to each annual meeting, the Secretary shall mail to all Members, of whatever class, an announcement of the time and place of the coming meeting.

The Treasurer shall deposit the funds of The Division only in banks and securities approved by the Executive Committee. The Treasurer shall be bonded for an amount determined from time to time by the Executive Committee.

5. EXECUTIVE COMMITTEE. There shall be an Executive Committee consisting of the Officers, the Editor of *Rubber Chemistry and Technology,* the Advertising Manager of *Rubber Chemistry and Technology* and five (5) Directors. The duties of the Executive Committee shall be as herein provided and as hereafter deter-

mined by The Division from time to time, and they shall perform the duties and assume the responsibilities ordinarily associated with such a committee.

The Officers of The Division shall be the Officers of the Executive Committee.

Each Director shall have the privilege of nominating one alternate, who is a Member of The Division, to represent him throughout any meeting of the Executive Committee, subject to the approval of the Chairman.

The Executive Committee shall meet at least twice each year. Meetings shall be held at the time and place of The Division meetings, except that the meetings of the Executive Committee shall precede the meetings of The Division.

Seven (7) members of the Executive Committee shall constitute a quorum.

6. ELECTIONS. All elections shall be by secret ballot. The Chairman shall not be eligible for election for the ensuing year.

Three of the five Directors shall be elected by The Division for a term of one year, starting at the close of the annual meeting at which the election is held. The outgoing Chairman and the defeated nominee for Vice-Chairman receiving next to the largest number of votes for that office shall be Directors for the ensuing year. No Director shall be eligible for reëlection as a Director for the ensuing year. Each Member shall vote for not more than three (3) nominees for Director. The three nominees for Director receiving the largest number of votes shall be declared elected. In the event of an indecisive vote because of a tie, those nominees receiving the same number of votes shall be voted upon until the tie is removed.

After receiving the Report of the Nominating Committee, the Chairman shall call for nominations from the floor.

In the event The Division does not hold a fall meeting, or no quorum is present at such meeting, the Executive Committee shall provide for a mail ballot.

7. "RUBBER CHEMISTRY AND TECHNOLOGY." *Rubber Chemistry and Technology* (hereinafter referred to as "The Journal"), shall be published by The Division.

The Editor and Advertising Manager shall be appointed by the Chairman, subject to the approval of the elected members of the Executive Committee. Any such action shall be effective for no longer than one year, and each shall serve until his successor is appointed.

The Editor shall publish The Journal from time to time during the year, in the name of The Division. He shall submit a budget for the following half of the calendar year to the Treasurer in writing, at least thirty (30) days before each regular meeting of the Executive Committee, and the Treasurer shall send copies of the same to each member of said Committee before the meeting.

The Advertising Manager shall submit an estimate of the revenue to be expected during the following half of the calendar year to the Treasurer in writing at least thirty (30) days before each regular meeting of the Executive Committee, and the Treasurer shall send copies of the same to each member of said Committee before the meeting.

The Editor and Advertising Manager shall absent themselves from Executive Committee meetings during discussions of the respective appointments of the Editor and Advertising Manager of The Journal.

The Division shall neither publish nor sponsor any other publication except on the approval of the Executive Committee and under the terms prescribed by them.

8. BUDGET. Ten days prior to each regular meeting of the Executive Committee, the Treasurer shall submit to each member of the Committee a proposed

budget covering all contemplated expenditures for the following half of the calendar year.

The Executive Committee at each regular meeting shall adopt a budget for The Division for the following half of the calendar year.

The Treasurer shall pay out no funds of The Division in excess of said budget until ten (10) days after mailing notification to each member of the Executive Committee of the fact that the budget is to be exceeded, and no funds shall be paid in excess of the budget in the event that the Treasurer receives a written protest from three (3) members of the Executive Committee within ten (10) days of the date of said mailing, exclusive of Saturdays, Sundays, national holidays and the date of mailing.

9. MEETINGS. Regular meetings of The Division shall be held at the times and places specified by the National Society unless otherwise determined by the Executive Committee. The annual meeting of The Division shall be in the fall of the year.

Fifty (50) Members shall constitute a quorum for any business meeting of The Division, except that no election shall be held unless one hundred (100) Members are present.

10. APPOINTED COMMITTEES. The Chairman shall appoint the following committees, and such other committees as from time to time he may deem best. These committees shall report at the annual meeting of The Division unless otherwise provided.

A. Nominating Committee. A Nominating Committee of five (5) members shall be appointed at least sixty (60) days prior to the annual meeting. This committee shall select at least one nominee for each office to be voted on at the coming meeting, and at least two nominees for Vice-Chairman.

B. Auditing Committee. An Auditing Committee of three (3) members shall be appointed who shall make an annual audit of the books of The Division.

C. Membership Committee. A Membership Committee of at least fifteen (15) members shall be appointed.

D. Crude Rubber Committee. A Crude Rubber Committee of at least five (5) members shall be appointed to study problems relating to control and use of crude rubber and latex and problems related thereto.

E. Nomenclature Committee. A Nomenclature Committee of at least five (5) members shall be appointed to consider and make recommendations to The Division relative to naming of materials, and terminology used by the Rubber Industry.

11. PLANNING COMMITTEE. The Planning Committee shall comprise the Chairman, the outgoing Chairman, the Vice-Chairman, the Secretary and such Members as the Chairman shall appoint thereto. The Vice-Chairman shall be Chairman of this Committee.

The Committee shall make recommendations for future meetings and programs, symposia, special programs, etc., such as will increase the value of The Division to its Members, the American Chemical Society and the public. At any meeting of The Division, the Committee may submit for adoption a plan for any future meeting.

12. FISCAL YEAR. The fiscal year of The Division shall end December 31.

13. RESPONSIBILITY. The Division is not responsible for statements and opinions advanced by individuals in papers, or discussions before its meeting.

No contract or agreement is binding on The Division unless approved by the Executive Committee.

14. AMENDMENT OF BY-LAWS. These By-Laws shall be amended only by a two-thirds (⅔) vote of the Members present at any regular meeting of The Division on recommendation of the Executive Committee. Amendments may be proposed by any Member by submission in writing to the Secretary, and when so submitted the Secretary shall refer said amendment to the Executive Committee. The Executive Committee shall consider same and make recommendations to The Division at its next regular meeting.

THE CHARLES GOODYEAR LECTURE

Founded by The Division of Rubber Chemistry of the American Chemical Society in commemoration of the One-Hundredth Anniversary of the Discovery of the Vulcanization of Rubber by Charles Goodyear.

RULES GOVERNING LECTURE

1. The Charles Goodyear Lecture may be given annually, at the discretion of the Lecture Committee, for the purpose of stimulating interest in fundamental research on rubber and to recognize those who have made outstanding contributions to the science of rubber or related subjects.

2. The Lecture shall be given before The Division at one of its regular meetings.

3. The Lecture Committee shall be a standing committee composed of seven past chairmen of The Division who are active members of The Division.

a. Chairman: The Chairman shall be the immediate past chairman of The Division.

b. Members: The membership shall be selected from the next most immediate past chairmen. Each year the oldest member of the Committee in point of service as Chairman of The Division shall be retired from the Committee. The membership of the Committee is therefore constituted each year following the election of officers and Executive Committee of The Division at its fall meeting. Vacancies due to inability of persons designated to serve may be filled by the Chairman of the Committee from the list of past chairmen. If a member of the Lecture Committee is nominated for lecturer, the Secretary of The Division shall serve in his place until final selection is made.

4. The function of the Lecture Committee is to select a Lecturer and to make the necessary arrangements for the Lecture. The Chairman of the Lecture Committee shall have the authority to deal directly with the lecturer in all matters concerning the Lecture.

5. Nominations for the lecturer may be sent to the Secretary of The Division by any member of The Division. Nominations shall be accompanied by a statement setting forth the qualifications of the nominee, with specific reference to the research on which the nomination is based. This statement should be in the form of seven copies, for distribution to the members of the Lecture Committee. All nominations to be considered must have been received by the Secretary of The Division on or before November 15 of the year prior to the Lecture.

6. Members of the Lecture Committee shall be uninstructed, and left solely to their own judgment in voting.

7. *a.* The Chairman of the Committee, before February 1, shall send each member a copy of these rules and a list of all candidates, and the reason for their nominations, presenting these in the form of the statements submitted by their proposers, but the names of the latter shall not be given.

b. The Chairman shall request a letter ballot. The candidate receiving five votes shall be considered elected. In case a choice shall not have been made on

the first ballot, the condidates receiving the highest two ballots shall be voted on again in a second ballot.

8. The Lecturer shall be notified of his selection prior to March 1.

9. The Lecturer shall be given an honorarium of $200.00 drawn by the Treasurer of The Division and presented by the Chairman ten days prior to the Lecture.

10. The Lecturer shall also be presented with a suitably inscribed certificate stating that he was the Charles Goodyear Lecturer.

11. The Lecture Committee shall have the power to decide any question not specifically covered by these rules.

12. These rules may be amended by a majority vote of The Division at any meeting, provided that written notice of the proposed amendment has been sent to each member of The Division at least thirty days in advance of the meeting.

NEW BOOKS AND OTHER PUBLICATIONS

1939 RUBBER RED BOOK—DIRECTORY OF THE RUBBER INDUSTRY. Published by THE RUBBER AGE, 250 West 57th St., New York. 6×9 in. 420 pp. $4.00 paper-bound; $5.00 cloth-bound.

With all former sections completely revised and widened in scope, and the addition of four new sections, the latest edition of this Directory of the Rubber Industry should prove even more valuable to the trade than was the previous—and initial—issue, published in 1937. The four new sections are: (1) Sales Agents and Suppliers' Branch Offices; (2) Technical Journals; (3) Technical and Trade Organizations; and (4) Who's Who in the Rubber Industry.

Other sections, all of which contain more detailed information than the previous issue, include: Rubber Manufacturers in the United States; Rubber Manufacturers in Canada; Rubber Machinery and Equipment; Rubber Chemicals and Compounding Materials; Fabrics and Textiles; Crude Rubber; Reclaimed Rubber; Scrap Rubber Dealers; Miscellaneous Types of Rubber and Allied Materials; Rubber Latex; Miscellaneous Products; Consulting Technologists.

Those sections which lend themselves to break-downs, such as rubber manufacturers, machinery, chemicals, fabrics, etc., are again handled in that manner. For instance, the rubber manufacturers section is divided into three parts, *i.e.*, an alphabetical list, a classified list of rubber products and a geographical section. The chemical section consists of a classified list of materials, a trade and brand name division and an alphabetical list of suppliers. The machinery and fabric sections are divided into classified and alphabetical lists.

One improvement which should prove important is the inclusion of an alphabetical subject index. Use of this index permits the user of the Directory to readily secure the exact type of information he is seeking. [From *The Rubber Age* of New York.]

RUBBER INDUSTRY OF THE UNITED STATES—1839-1939. By P. W. Barker. Bureau of Foreign and Domestic Commerce, Washington, D. C. 6×9 in., 42 pp., 10c (from Superintendent of Documents, Washington, D. C.).

Issued in commemoration of the 100th anniversary of the discovery of vulcanization by Charles Goodyear in 1839, this booklet traces the birth and development of the American rubber manufacturing industry. Rubber cultivation methods and rubber manufacturing processes are briefly discussed, and the world position of the United States is stressed. One section is devoted completely to statistics, based largely on data made available by the Bureau of the Census

through the years. The final section is devoted to the varied uses of rubber, including the importance of the commodity in modern affairs, its versatility and specialized uses. Of special interest is an alphabetic list of rubber products, one of the most comprehensive made available to date. A number of tables showing trends in the rubber industry is also included in the booklet. [From *The Rubber Age* of New York.]

SECOND REPORT OF THE RUBBER-FOUNDATION COVERING THE PERIOD JANUARY 1-DECEMBER 31, 1938. Rubber-Stichting, Heerengracht 182, Amsterdam-C, Netherlands, 128 pages.

In this second report a survey of the administrative, technical and propaganda activities of the Rubber Foundation, the Dutch organization for furthering the use of rubber, is presented. The more important activities of the Research Department during the period under review included studies on the following: asphalt-rubber powder mixes; latex-colloidal clay systems; properties of latex and latex compounds; vibration damping; bonding of rubber to other materials; synthetic rubbers. The appendices at the end of the book cover certain revisions in the International Rubber Regulation Agreement; balance sheet of the Rubber Foundation; and work programs for 1939 of the Rubber Foundation and the Experimental Station, West-Java Department, Buitenzorg. [From the *India Rubber World.*]

RUBBER PRODUCING COMPANIES—1939. Mincing Lane Tea and Rubber Share Brokers' Association, Ltd. Plantation House, Mincing Lane, London, E.C. 3, England. 5½×8 in., 580 pp., 8s 1d (approximately $2.00).

The latest edition of this manual gives particulars of approximately 600 rubber-planting companies, including such data as forward sales, capitalization, investments and reserves. A valuable feature is the analyses of results of each company for the past few years. The analyses show estate areas (budded and other), standard outputs, annual production, gross price, "all-in" cost, net profit, dividend and carry-forward. The date of the last reports and annual meetings are also given. The edition has been completely revised. [From *The Rubber Age* of New York.]

INDIA RUBBER MAN. Ralph Wolf. Published by The Caxton Printers, Ltd., Caldwell, Idaho. 1939. Cloth, 6×9 in., 291 pages. Bibliography and subject index. Price $3.

This book is more than a chronicle of historical facts; it is a story of definite human interest about a man who ranks among the foremost of American inventors. Written by the co-author of "Rubber, A Story of Glory and Greed," this is the first extensive biography of Charles Goodyear, discoverer of vulcanization and, as such, founder of the rubber industry, to appear in book form. The publication of "India Rubber Man" is timely, for it was just a century ago that Goodyear made his momentous contribution to the rubber world.

Mr. Wolf has searched the literature well in providing a comprehensive historical record of Goodyear's life, but in so doing he has not sacrificed reader interest. Although the author's style tends toward the dramatic, the book is well written, and at no time is the continuity of the story lost; yet it is packed with interesting anecdotes about Goodyear and his contemporaries. Several chapters deal with the inventors' forebears, his early life, and a brief early history of rubber. The main part of the book is concerned with Goodyear's

experiments with rubber, his privations, his epochal discovery, and the bitter years that followed. Legal and financial difficulties are treated in detail. One chapter borrows heavily from Goodyear's own book, "Gum-Elastic," in which are enumerated the many applications for rubber. Nowhere does the author lose sight of the inventor's enthusiasm, which persisted even in the face of poverty, hunger and almost unsurmountable difficulties. "India Rubber Man," a story of an unfaltering devotion to the cause of rubber, can be read with interest and profit by all, and should be read by every one connected with the rubber industry. [From the *India Rubber World*.]

FIRST REPORT ON VISCOSITY AND PLASTICITY. Second Edition. Prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. Nordemann Publishing Co., Inc., 215 Fourth Ave., New York, N. Y. 1939. Cloth, 7×10¼ in., 273 pages. Indexed. Price $7.

The first edition of this report on viscosity and plasticity appeared in 1935. In this second impression a few minor changes have been introduced, and there have been added references to passages of the "Second Report on Viscosity and Plasticity" (published in April, 1938), where this seemed useful, and to some papers of importance not mentioned in the original edition or having appeared after its publication. Certain additions of greater extent have been prepared by H. J. Jordan for the chapter on viscosity effects in living protoplasm and in muscles. An index has been added to the volume.

The subject matter, which covers the same ground as the first edition, deals with basic theoretical concepts involved in the processes of deformation; experimental investigation of flow properties; technique of viscosity measurements; technical aspects of viscosity and plasticity, including a discussion on rubber; plastic deformation of crystalline substances, and viscosity effects related to biology. [From the *India Rubber World*.]

PROPOSED REVISION OF FEDERAL SPECIFICATION [ZZ-R-601] FOR RUBBER GOODS: GENERAL SPECIFICATIONS (Methods of Physical Tests and Chemical Analyses). United States Department of Commerce, National Bureau of Standards, Washington, D. C. 43 mimeographed pages. Illustrated.

This suggested revision of this specification, long and widely used in the industry, available free of charge by writing the National Bureau of Standards, is for comment only. Suggestions will be welcomed and given careful consideration. The actual revision will not be made until government purchasing agencies, manufacturers and others interested have had full opportunity to express opinions and prepare recommendations. [From the *India Rubber World*.]

RUBBER AND LATEX IN FURNISHING AND DECORATION (A Reprint). British Rubber Publicity Association, 19 Fenchurch St., London, E.C. 3, England. 9¼×12½ in., 28 pp.

Reprinted from a recent issue of the *Furnishing Trades' Organiser*, this booklet traces the growing use of rubber and latex in the furnishing and decoration arts. Uses in the home, public buildings, ships, stores and theatres are described and capably illustrated. There is also a section devoted to a description of the raw material. Copies of the booklet can be secured in this country from the Crude Rubber Development Bureau, Munsey Building, Washington, D. C. [From *The Rubber Age* of New York.]

SIGNIFICANCE OF ACCELERATED AGING TESTS FOR RUBBER. (Report No. 39-4.) By Arthur M. Neal. Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. 6¼×9¼ in., 12 pp.

This report is devoted to a survey of the various accelerated aging tests, including the Geer Oven Aging Test, the Oxygen-Bomb Aging Test, the Modified Oxygen-Bomb Test, and the Air Pressure Heat Test. The causes of deterioration on aging are discussed, as are the fundamental requirements of an accelerated aging test. The scientific background for the development of an accelerated aging test is also given consideration. As indicated by the title of the report, the author stresses the significance of the tests. [From *The Rubber Age* of New York.]

RUBBER EQUIPMENT IN MODERN FARM MANAGEMENT. By D. N. McHardy. British Rubber Publicity Association, 19 Fenchurch St., London, E.C. 3, England. 5½×8½ in., 20 pp.

Prepared by the Chairman of the Tractor Users' Association, Ltd. (of England), this booklet is the eleventh in the series of bulletins on the uses of rubber in agriculture issued by the British Rubber Publicity Association. As indicated by the title, the uses of pneumatic tires on modern farm vehicles of all types are illustrated and described. Copies of this booklet may be secured in this country from the Crude Rubber Development Bureau, Munsey Building, Washington, D. C. [From *The Rubber Age* of New York.]

RUBBER AS AN ENGINEERING MATERIAL. The B. F. Goodrich Co., Akron, O. Cloth, 8½×11 in., 25 pages.

Written for men who are dealing with materials and designing products, this handbook presents brief but concise information about rubber—its various forms, its properties and limitations. Considerable space is devoted to the resistance of rubber to corrosion, abrasion, cutting, tearing, impact, heat, oil and solvents. The elasticity of rubber and its use for vibration, shock and noise isolation are discussed. One chapter deals with a comparison of the properties of the firm's elastic synthetics with the properties of rubber. [From the *India Rubber World.*]

TRUCK AND BUS TIRE SERVICE MANUAL. The B. F. Goodrich Co., Akron, O. 16 pages.

This manual on truck and bus tires, designed to assist users in overcoming premature tire failure, points out the common causes of such failure: excessive tread wear, crown breaks and abnormal heat generation. Contributing factors in length of tire life: load carried, distribution of weight, operating speeds, road surface conditions and atmospheric temperature are discussed; also the importance of correct tire type and size, proper inflation and equally mated tires on dual installations is stressed. [From the *India Rubber World.*]

USES AND APPLICATIONS OF CHEMICALS AND RELATED MATERIALS. Compiled and Edited by Thomas C. Gregory. Reinhold Publishing Corp., 330 West 42nd St., New York City. 6×9 in., 653 pp., $10.00.

This book contains surveys on the uses, potential applications and sales possibilities of more than 5,000 chemicals and related materials. These surveys have been appearing in the pages of the *Oil, Paint & Drug Reporter* since 1922, originally under the title "Where You Can Sell," but more recently under "Industrial Uses of Chemicals and Related Materials." The surveys have been rearranged,

amplified and completely edited by Mr. Gregory, an expert on chemical marketing, so that the material in its present form represents a mass of information unavailable elsewhere. Among materials presented are inorganic chemicals, organic chemicals, mineral acids, organic acids, fine chemicals, and drug and pharmaceutical products. All products are arranged in strict alphabetical order and not by chemical classification. A list of synonyms and cross-references is included. [From *The Rubber Age* of New York.]

HANDBOOK OF CHEMISTRY AND PHYSICS—23RD EDITION. Edited by Charles D. Hodgman. Chemical Rubber Co., 1900 West 112th St., Cleveland, Ohio. $7\frac{1}{8} \times 4\frac{3}{4}$ in., 2240 pp., $3.50 (Regular Edition); $6.00 (DeLuxe Edition).

Approximately 400 pages larger than the previous issue, this newest edition of the increasingly valuable Handbook contains a substantial amount of new information concerning compounds already listed and a considerable number of new compounds. The general plan of the book has been retained with minor exceptions. Like previous editions, the latest data available on chemistry, physics, mathematics and related sciences are presented. The 11 sections of the book are divided into the following groupings: Mathematical Tables, Properties and Physical Constants, General Chemical Tables, Specific Gravity and Properties of Matter, Heat, Hygrometric and Barometric Tables, Sound, Electricity and Magnetism, Light, Quantities and Units, and Miscellaneous. A complete subject index is included. [From *The Rubber Age* of New York.]

ABRIDGED SUMMARY OF REPORTS OF THE CRUDE RUBBER COMMITTEE OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

Since the inception of the Crude Rubber Committee of the Division of Rubber Chemistry, reports have been made regularly to the Division at the semiannual meetings of the Society. However, these reports are not readily accessible, and hence it seemed desirable to publish the seven reports to date in condensed form, with references to the complete reports when published.

Report No.	Date and Place	Subjects	Published
I	Sept. 30-Oct. 1, 1935 (Akron, Ohio)	Proposed testing recipe	Official report in *Rubber Age* (N. Y.) **38**, 33 (Oct. 1935). News item in *India Rubber World*, **93**, No. 2, 49 (Nov. 1935).
II	April 16, 1936 (Kansas City, Mo.)	Tentative testing recipe	Official report in *Ind. Eng. Chem., News Ed.* **14**, 215 (June 10, 1936) and *Rubber Age* (N. Y.) **39**, 157 (June 1936).
III	Sept. 10, 1936 (Pittsburgh, Pa.)	Testing recipe; data on several rubbers; copper and manganese; plasticity	News item in *Rubber Age* (N. Y.) **39**, 841 (Sept. 1936) and *India Rubber World* **95**, No. 1, 55 (Oct. 1936).
IV	April 14, 1937 (Chapel Hill, N. C.)	Copper and manganese procedures	News summary in *Rubber Age* (N. Y.) **41**, 109 (May 1937). News item in *India Rubber World* **96**, No. 2, 59 (May 1937).
V	Sept. 8, 1937 (Rochester, N. Y.)	Latex specifications; plasticity	Official report in RUBBER CHEM. TECH. **10**, p. xxviii (Oct. 1937). News item in *Rubber Age* (N. Y.) **41**, 883 (Sept. 1937) and *India Rubber World* **97**, No. 1, 57 (Oct. 1937).
VI	Mar. 28, 1938 (Detroit, Mich.)	Dirt; plasticity; discussion of Page's six questions	Brief official report in *Ind. Eng. Chem. News Ed.* **16**, No. 9, 266 (May 10, 1938). News summary in *Rubber Age* (N. Y.) **42**, 375 (Mar. 1938); **43**, 39 (Apr. 1938), and *India Rubber World* **98**, No. 2, 55 (May 1938).
VII	April 5, 1939 (Baltimore, Md.)	Adoption of latex procedures	News summary in *Rubber Age* (N. Y.) **45**, 34 (Apr. 1939) and *India Rubber World* **100**, No. 2, 45 (May 1939).

REPORT I

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY IN AKRON, OHIO, SEPTEMBER 30–OCTOBER 1, 1935

Committee: E. B. BABCOCK, W. A. GIBBONS, HAROLD GRAY (Chairman), G. A. SACKETT, J. C. WALTON

The Crude Rubber Committee was appointed by S. M. Cadwell, Chairman of the Division, at the New York meeting of the American Chemical Society, April 23, 1935. The function of the Committee was to promote a better understanding between the producer and the consumer of crude rubber.

After a preliminary meeting in New York, April 23, 1935, a second meeting was held in Akron, April 27, 1935. Edgar Rhodes of the Rubber Research Institute of Malaya was present and gave the Committee some very helpful suggestions on the general situation in the Far East.

The first action of the Committee was to define its scope of operation.

"The function of this committee is to promote a better understanding between the producers and consumers of crude rubber and to act as a clearing house between the two groups for information on the quality requirements for various crude rubbers, including latex; to exchange opinions on the value of new types of crude rubber, etc.

"The committee proposes to establish contacts with the various technical agencies allied with the producers on the matter of quality requirements, methods of testing, and evaluation of new types of rubber, including latex.

"The committee will concern itself only with technical aspects of the problem. The committee will deal only with those items, the information on which can be made public."

Then points of contact with organizations of producers were made:

Director of the West Java Proefstation, Buitenzorg, Java, Netherland East Indies.

Director A. V. R. O. S. Proefstation, Medan, E. C., Sumatra, Netherland East Indies.

Director Ceylon Rubber Research Scheme, Culloden, Neboda, Ceylon.

London Advisory Committee for Rubber Research, Imperial Institute, South Kensington, London, S. W. 7, England.

Director Rubber Research Institute of Malaya, Kuala Lumpur, Federated Malay States.

A. L. Viles, Rubber Manufacturers' Association, 444 Madison Avenue, New York, N. Y.

The Rubber Growers' Association, 19 Fenchurch Street, London, E. C. 3, England.

Finally, plans were made for establishing definite test recipes and procedures for evaluating the variability of crude rubber.

REPORT II

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY IN KANSAS CITY, MISSOURI APRIL 16, 1936

Committee: E. B. Babcock, W. A. Gibbons, Harold Gray (Chairman), G. A. Sackett, J. C. Walton

A committee meeting was held at Akron, Ohio, March 30, 1936. The following tentative standard recipe was selected. This recipe is very similar to one under consideration by the British Standards Institution, and emphasizes deficiencies in fatty acid and also activation.

Tentative Standard Testing Recipe

(Variability in Curing Properties)

Rubber	100.
Zinc Oxide	6.
Sulfur	3.5
Stearic Acid	.5
Mercaptobenzothiazole	.5

Cure: 20, 30, 40, 60, 80 minutes at 260° F.

The testing procedure to be followed is that outlined by the American Society for Testing Materials, Committee D-11 (on Rubber Products) (1937 A.S.T.M. Standards on Rubber Products, Specification D412-36T, "Tension Testing of Rubber").

Tensile strength and elongation at rupture and moduli at 500, 600 and 700 per cent elongation may be reported.

Tabulated data (see Table I) on thirty-two different lots of No. 1 Ribbed Smoked Sheet, which have been tested in the Tentative Standard Recipe, show very clearly large differences in curing rates.

Also, tentative specifications for sulfur, zinc oxide, mercaptobenzothiazole and stearic acid for use in the Tentative Standard Testing Recipe are given:

Sulfur (natural product):

Fineness	—100% through 100-mesh screen.
Moisture	—Not over 0.25% (2 hrs. at 105° C.).
Acidity	—Not over 0.01% (as H_2SO_4).
Ash	—Not over 0.10%.
Purity	—Not less than 99.5% soluble in carbon disulfide.

Zinc Oxide:

Free from grit.

Fineness	—100% through 100-mesh screen. 99.85% through 300-mesh screen.
Moisture	—Not over 0.40% (2 hrs. at 105° C.).
Sp. gravity	—5.60-5.65.
Lead	—Not over 0.10% (as PbO).
Copper	—Not over .001%.
Manganese	—Not over .003%.
Sulfur	—Not over 0.25% (SO_3).

99.75% soluble in 10% acetic acid solution.

Mercaptobenzothiazole:

Purity	—Not less than 91% mercaptobenzothiazole (titration with alkali).
Fineness	—100% through 100-mesh screen.
Melting point	—Minimum 165° C.
Ash	—Not over 0.50%.
Heating loss	—Not over 1.00% (2 hrs. at 105° C.).

Stearic Acid:

Double-pressed from animal fat.

Titer	—Not less than 52° C.
Acid Number	—185 to 200.
Iodine Number	—Not over 10.

The Committee feels that the reports and discussions at the New York and Akron meetings of The Division of Rubber Chemistry, in addition to the information contained in this report, are sufficient as far as presenting the problem of variability in curing properties of rubber to the producers is concerned. For the time being, at least, all that the Committee can do is to continue to coöperate with producers' technical organizations, as any improvements that may be made must necessarily result from efforts of the producers.

Several other items have been presented to the Committee for consideration. These include aging, plasticity, packaging, cleanness, etc. All these items have been given consideration by the Committee, but no definite recommendations are ready at the present time. A brief résumé of the situation on each is given.

Each of the Committee members will study the aging data available and

TABLE I

No. 1 RIBBED SMOKED SHEET TESTED IN THE TENTATIVE RECIPE OF THE CRUDE RUBBER COMMITTEE

Sample No.	Cure 20 min. at 260° F.					Cure 30 min. at 260° F.					Cure 40 min. at 260° F.					Cure 60 min. at 260° F.					Cure 80 min. at 260° F.				
	Tensile *	Elongation	500%	600%	700%	Tensile *	Elongation	500%	600%	700%	Tensile *	Elongation	500%	600%	700%	Tensile *	Elongation	500%	600%	700%	Tensile *	Elongation	500%	600%	700%
58	150	900	Not recorded			1500	925	150	300	500	1850	915	200	350	675	2550	900	300	500	975	2750	875	300	575	1175
50	500	1000	Not recorded			1675	935	200	325	525	1800	875	300	425	800	2600	865	325	525	1075	2900	855	375	650	1250
52	500	975	Not recorded			1700	930	150	300	500	2000	870	250	425	800	2500	870	300	500	1000	2700	860	325	575	1150
60	700	1060	Not recorded			2000	925	250	400	700	2400	880	275	500	1000	2875	850	400	700	1300	3300	875	400	750	1400
48	1600	940	175	300	500	2100	900	300	500	900	2450	845	325	600	1200	2625	825	350	675	1300	3000	830	400	800	1525
49	1925	900	200	350	650	2400	910	300	500	950	2550	890	325	600	1100	2650	860	325	600	1275	3100	865	400	750	1450
61	1750	960	200	325	525	2550	900	300	500	900	2750	855	350	650	1325	3200	850	400	800	1575	3350	840	425	800	1575
39	2200	985	200	375	700	2500	890	300	550	1000	2750	850	350	650	1275	3100	840	400	750	1550	3400	855	450	850	1650
46	1850	900	200	400	750	2700	895	300	550	1100	2800	860	325	675	1350	3300	880	350	750	1550	3175	840	400	800	1600
37	2300	920	250	400	775	3000	895	300	425	1200	2775	845	350	675	1375	3200	830	400	700	1500	3400	830	450	875	1750
63	2000	900	250	450	800	2400	885	350	600	1100	2600	850	400	700	1300	3300	850	450	800	1500	2900	835	450	800	1500
38	2500	930	225	400	825	2850	865	325	600	1275	3100	845	350	700	1500	3550	840	425	875	1775	3100	800	450	950	1900
55	2000	900	250	400	800	2550	875	325	650	1250	2750	825	400	750	1400	3250	830	425	700	1500	3050	800	550	1050	2050
69	1750	850	300	500	925	2175	870	300	500	1025	2450	800	400	775	1500	2800	785	500	925	1775	3100	785	550	1025	1900
64	2300	930	250	475	900	2450	840	375	650	1275	2000	835	450	774	1470	3000	825	450	825	1700	3275	845	500	925	1875
70	1800	880	225	400	800	2175	810	325	600	1175	2550	810	400	800	1625	2950	790	500	1000	1925	3200	800	550	1050	2025
47	2300	900	250	475	100	2875	880	300	600	1225	3200	850	400	800	1500	3325	845	425	900	1775	3300	800	500	1000	1975
44	2400	890	300	450	700	2800	870	375	625	1200	3125	845	425	800	1500	3450	830	475	900	1775	3325	815	550	1050	1900
68	2300	860	325	625	1200	2600	830	400	800	1425	2875	810	450	850	1650	3100	800	550	1100	2050	3350	790	600	1200	2200
51	2600	870	300	575	1125	3100	845	375	725	1450	3250	825	425	850	1650	3375	830	425	875	1750	3325	800	500	1025	2025
59	2075	880	300	475	900	2650	845	400	750	1400	2900	800	500	900	1725	2775	760	575	1075	2050	3400	870	600	1100	2000
43	2700	965	350	675	1300	3150	840	400	800	1500	3600	840	500	900	1850	3450	790	575	1100	2100	3350	785	600	1200	2325
57	2100	875	300	525	975	2575	810	425	825	1550	2575	780	500	950	1725	3225	800	525	1050	2000	3400	800	550	1100	2050
56	2550	860	375	700	1350	3050	815	450	900	1750	3100	810	500	975	1800	3450	790	550	1100	2125	3600	800	600	1200	2375
66	2450	875	250	500	1000	2950	800	400	875	1725	3200	785	475	1025	2025	3300	770	550	1175	2300	3500	770	600	1250	2400
45	2450	865	375	650	1175	3100	845	500	925	1675	3250	820	550	1050	1850	3500	800	650	1250	2150	3650	800	700	1275	2425
54	2450	835	375	700	1300	2925	800	500	1025	1850	3000	800	550	1075	2000	3425	800	650	1225	2325	3575	790	700	1400	2500
62	2475	820	425	850	1475	2525	765	600	1150	1925	3150	790	575	1100	2125	3450	790	650	1275	2325	3300	765	650	1300	2450
65	2750	800	425	900	1650	3025	775	550	1100	2050	3200	765	600	1200	2250	3450	770	650	1300	2500	3350	760	600	1250	2425
27	2875	805	475	900	1750	3150	795	550	1075	2050	3450	790	625	1225	2250	3725	785	700	1425	2700	3250	720	800	1600	2950
53	3200	855	400	800	1525	3500	825	475	1000	1975	3375	770	600	1275	2500	3800	795	650	1350	2600	3800	775	700	1400	2900
67	2650	835	400	800	1400	3000	790	600	1150	2000	3000	750	625	1325	2275	3475	755	750	1500	2675	3275	725	800	1575	2825
Ave.	2060	895				2620	855	370	700	1315	2820	830	435	825	1575	3180	820	490	945	1785	3265	810	535	1015	1985

Arranged in order of modulus at 600% for the 40 min. at 260° F. cure.

* The tensile strengths and moduli at the three percentage elongations are in lbs. per sq. in.; the ultimate elongations are in percentages at rupture.

methods used in his own particular laboratory. The information from each of the laboratories is to be checked by all members of the Committee and from this information a definite program will be outlined.

Before a definite report of any kind can be made on the subject of plasticity, it will be necessary to make a very careful survey of all the various methods of determining plasticity now in use. A definite fundamental starting basis will have to be determined, and unanimous agreement, among the Committee members at least, obtained as to what properties should be studied in determining plasticity before recommendations to the Division of Rubber Chemistry can be made.

The Committee can do very little in the matter of cleanness except to urge that the entire industry insist on receiving uniformly clean rubber. We know definitely from our contacts with the Far East that this item is being given considerable attention on the plantations.

As far as packaging is concerned, very little can be done because of the present system of marketing rubber. However, one statement can be made, namely, that bales are preferable to cases as far as cleanness is concerned.

The Committee is checking the general situation on latex, and may find it advisable to study certain phases; but at the present time it is not in a position to report any progress.

Since the Committee is operating without funds, the amount of work done must necessarily be limited, and the amount of time involved will be considerable, involving years rather than months. The problems investigated must necessarily be general and broad, and involve the industry as a whole. Specific problems dealing with some particular branch of the industry cannot be considered.

The Committee wishes to express its appreciation to those who have offered to assist in this work and to urge that other members of the Division of Rubber Chemistry send in any available data related to the various problems under consideration.

In particular the Committee wishes to express its appreciation to the various organizations and individuals on the producing side of the crude rubber industry who have offered to coöperate.

The Committee is very pleased to announce that they are in receipt of a communication signed by L. R. van Dillen of the A.V.R.O.S. Proefstation, who has written in the capacity of Secretary of a Crude Rubber Committee which has just been set up in the Dutch East Indies. This committee has been formed with the express purpose of coöperating with the Crude Rubber Committee of the Division of Rubber Chemistry of the American Chemical Society in an effort to promote better understanding between consumers and producers.

The personnel of the committee in the Dutch East Indies is as follows:

W. T. L. ten Broock..... The Goodyear Rubber Plantations Company.
W. E. Cake..... Hollandsch-Amerikaansche Plantage Mij.
L. R. van Dillen..... A.V.R.O.S. Proefstation, Secretary.
Th. G. E. Hoedt..... West-Java Proefstation.
H. van der Meyden (Chairman)..... Rubber Cultuur Mij. Amsterdam.

REPORT III

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY IN PITTSBURGH, PENNSYLVANIA, SEPTEMBER 7-11, 1936

Committee: E. B. Babcock, W. A. Gibbons, Harold Gray (Chairman), G. A. Sackett, J. C. Walton

Six methods for the determination of manganese and five for the determination of copper in crude rubber have been studied. To date, the Committee has been unable to agree on standard methods. However, as soon as an agreement is reached, copies of the method will be sent to the Rubber Research Institute of Malaya, at whose request the work was started.

The Committee has approved the Bulletin of Committee D-11 on Rubber Products, of the American Society for Testing Materials, published in October 1935, and recommends that the methods be used throughout the industry. It is understood, of course, that the Crude Rubber Committee agrees with the listing of methods as "standard" and "tentative," adopted by Committee D-11. There are a few items in this bulletin with which the Crude Rubber Committee is not in exact agreement, but these can be worked out later.

During the past few months, the Committee has done a great deal of work on the plasticity of crude rubber. Five samples of No. 1 ribbed smoked sheet were sent from each laboratory to each of the other four laboratories of the Committee members. This made a total of 25 samples. The samples were checked by six methods: Firestone extrusion, Goodrich, United States Rubber Products, Williams, modified Williams, and Boston Woven Hose and Rubber Co. This study brought out two points very clearly: (1) there is considerable variation in the plasticity of No. 1 ribbed smoked sheet (this is shown by all of the methods), and (2) the various methods of determining plasticity do not necessarily line up a series of samples in the same order. Plasticities were run on the crude rubber as well as on the same rubbers after various periods of mastication. Mastication did not smooth out the variations in plasticity. The data on the plasticity work are not published in this report, since nothing definite can be recommended at present as a standard method of determination.

Enough work has been carried out to show that there is no correlation between light and dark sheet and slow- and fast-curing rubber. Table II shows the results obtained on four samples of dark and five samples of light colored rubber. The Crude Rubber Committee recipe was used.

Plasticities (Goodrich plastometer) were run on a series of light and dark colored sheet. Again, no correlation was noted. Table III gives the results.

The Committee has carried out some work on aging but is not yet ready to report.

The Committee wishes to express its appreciation to Col. B. J. Eaton, who is retiring as Director of the Rubber Research Institute of Malaya, for his assistance.

The Committee also wishes to congratulate H. J. Page on his appointment to the Directorship, succeeding Colonel Eaton.

Table II

Tensile Strengths, Breaking Elongations and Tensile Moduli of Smoked Sheet Tested in the Crude Rubber Committee Recipe

Sample No.	Cure 20 min. at 260° F.					Cure 30 min. at 260° F.				
	Tensile	Elongation	500%	600%	700%	Tensile	Elongation	500%	600%	700%
73 (Dark)	2250	915	250	425	800	2400	875	300	600	1075
74 (")	1850	920	225	375	700	2300	890	300	550	1025
84 (")	2450	900	300	500	1000	2550	875	325	700	1200
86 (")	1850	900	225	375	700	2300	890	300	500	950
75 (Light)	2150	890	275	450	825	2525	875	300	525	1025
76 (")	2925	835	475	900	1600	3000	800	575	1100	1975
78 (")	2525	915	250	450	850	2800	855	325	600	1275
79 (")	2750	910	250	425	875	3250	880	325	600	1300
80 (")	2600	860	350	625	1150	3050	840	375	700	1400

Sample No.	Cure 40 min. at 260° F.					Cure 60 min. at 260° F.				
	Tensile	Elongation	500%	600%	700%	Tensile	Elongation	500%	600%	700%
73 (Dark)	2700	835	350	700	1300	3100	850	400	750	1475
74 (")	2600	865	350	775	1225	3075	850	450	800	1525
84 (")	3050	840	400	800	1525	3000	820	450	800	1500
86 (")	2450	870	350	575	1150	2700	835	400	700	1400
75 (Light)	2750	860	350	650	1275	2725	820	400	750	1450
76 (")	3150	775	700	1300	2275	3150	740	800	1500	2750
78 (")	3275	875	350	700	1325	3400	840	400	800	1600
79 (")	3350	840	400	675	1425	3500	830	450	825	1700
80 (")	3200	825	450	900	1700	3350	820	500	950	1750

Sample No.	Cure 30 min. at 260° F.				
	Tensile	Elongation	500%	600%	700%
73 (Dark)	2875	815	475	875	1650
74 (")	3225	845	475	900	1650
84 (")	3400	845	500	925	1750
86 (")	2900	820	475	800	1500
75 (Light)	3150	840	450	800	1500
76 (")	3350	740	900	1650	2950
78 (")	3475	840	450	875	1700
79 (")	3650	835	450	875	1750
80 (")	3600	825	550	1000	1900

The tensile strengths and moduli at the three percentage elongations are in lbs. per sq. in.; the ultimate elongations are in percentages at rupture.

Table III

Plasticity Values

Sample	Crude	Mastication 5 min.	10 min.	15 min.	Sample	Crude	Mastication 5 min.	10 min.	15 min.
73 (Dark)	3.20	15.9	31.4	49.3	75 (Light)	4.06	18.5	32.5	49.1
	3.74	15.5	33.3	48.8		3.80	17.8	32.8	50.0
74 (Dark)	5.92	21.6	34.5	49.5	76 (Light)	4.08	22.8	35.5	42.0
	4.26	19.4	32.8	50.4		4.85	20.4	34.7	40.2
84 (Dark)	2.85	15.0	25.9	30.7	78 (Light)	2.43	12.2	18.4	31.2
	2.97	14.2	25.5	31.3		2.50	14.4	19.9	28.0
86 (Dark)	2.49	13.1	19.3	25.7	79 (Light)	4.52	14.8	21.7	29.1
	2.35	12.7	20.5	27.0		3.85	15.7	23.6	28.6
					80 (Light)	3.78	17.5	21.1	25.6
						4.11	14.5	19.4	25.0

REPORT IV

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY AT CHAPEL HILL, NORTH CAROLINA, APRIL 14, 1937

Committee: E. B. Babcock, R. H. Gerke, Harold Gray (Chairman), G. A. Sackett, J. C. Walton

The Crude Rubber Committee has had two meetings since the divisional meeting in Kansas City, September, 1936. The first of these meetings was held in Akron, Ohio, October 19, 1936. The second meeting was held in New York City, January 28-29, 1937. The second day of the meeting in New York was devoted to a discussion of the manuscript "Specifications for Testing the Variability of Normal and Concentrated Latex." This meeting was attended by men, other than the committee, who are interested in latex.

The following paragraphs cover the activities of the Committee since the divisional meeting in Kansas City.

Methods for Determination of Copper and Manganese in Crude Rubber

The Committee was asked to establish methods for the determination of copper and manganese in crude rubber. After considerable work in the various laboratories, during which the methods used in these laboratories and various modifications of them were checked, satisfactory methods were finally agreed on. Copies of these various methods have been sent to interested parties in Europe and the Far East. It should be pointed out that these methods are to be used only with crude rubber. The procedure for copper is affected by an excess of iron. It is very unlikely, however, that this will have any detrimental effect, since the method is only for crude rubber.

These methods have been approved as tentative by A.S.T.M. Sub-Committee 11 of D-11, and are being restudied in coöperation with this Sub-Committee.

The methods follow:

Determination of Manganese in Crude Rubber

Ash a 10-gram sample in a large crucible at the lowest possible temperature. Start the ashing process on an open flame, slowly raise the temperature to a dull red heat, and then place in a muffle furnace at the same temperature for approximately one hour. After this ignition the residue may be gray or black. It is not necessary to continue the ignition to a white ash. Add 10 to 15 grams of potassium pyrosulfate to the ash, fuse cautiously until effervescence ceases, and then more strongly (low red heat) until all carbon particles are burned off. Cool and dissolve the melt in 80 to 100 cc. of 5% sulfuric acid.

Cool, add 5 cc. of concentrated phosphoric acid (85%, approximately 1.7 gravity), 15 cc. of concentrated sulfuric acid (1.84 gravity) and 20 cc. of concentrated nitric acid (1.42 gravity), cool, filter through asbestos, wash filter pad once with 10-15 cc. of concentrated nitric acid (1.42 gravity), place filtrate in a 250-cc. beaker, heat to 90-100°C., add 0.2 gram of sodium periodate, maintain at this temperature for 5 minutes, and dilute with water to 250 cc., whereupon the color appears. Compare this solution with a standard made up by dissolving 0.406 gram of manganese sulfate ($MnSO_4.4H_2O$) in 1000 cc. of distilled water. One cc. of this solution is equal to 0.0001 gram of manganese. This solution is used as a primary standard, so great care should be exercised in its preparation.

Place 1 cc. of standard manganese sulfate solution in a small beaker (250 cc.), add 5 cc. of concentrated phosphoric acid (85%, approximately 1.7 gravity), 15 cc. of concentrated sulfuric acid (1.84 gravity) and 20 cc. of concentrated nitric acid (1.42 gravity), heat to 90-100°C., add 0.2 gram of sodium periodate, heat for 5 minutes and dilute with water to 100 cc. The standard is then ready for comparison with the solution of the unknown.

Place an aliquot of 25 cc. of solution of the sample in a Nessler tube, measure from a burette varying volumes of the standard $HMnO_4$ solution, place in other Nessler tubes and dilute with water to the mark. In this manner, make a standard solution to match the color intensity of the sample.

Calculations:

$$\frac{(\text{cc. of standard}) \times (\text{g. Mn per cc.}) \times 10}{\text{wt. of sample}} \times 100 = \%\ \text{Mn}$$

Determination of Copper in Crude Rubber

Ash a 20-g. sample over a Bunsen burner and finally in a muffle furnace. Do not expose to a higher temperature than a dull red heat. Particles of carbon enclosed in the ash need not be burned off, as any portion of the copper existing as chlorides may be volatilized at the same time. Add 5 cc. of concentrated hydrochloric acid, heat the crucible until the acid boils, transfer by means of a fine stream of water and a rubber policeman to a small beaker, boil for a few minutes; after the solution has cooled, make it alkaline with NH_4OH, and heat on a steam plate until the volume of the solution is not more than 15 cc. (a steam plate is best for heating, as there is often danger of spattering). By this time, all of the excess ammonia will have been driven off. Add a few drops of bromine water, heat to boiling (see Note 1), filter immediately through a Gooch crucible into a graduated vessel (a graduated test-tube which will slide inside the usual suction filter flask serves the purpose nicely), dilute the solution to 30 cc., and place 10 cc. of the solution in a 50-cc. Nessler tube. If the copper concentration is high (.01%), use 5 cc. of solution; if the copper concentration is low, use 20 cc. of solution. Add 22.5 cc. of 95% pure ethyl alcohol and 2.5 cc. of a 1% solution of sodium diethyldithiocarbamate in 95% pure ethyl alcohol. Mix thoroughly.

For a standard (see Note 2), prepare a similar solution in a Nessler tube, using 10 cc. of water in place of the portion of the sample. Add a solution containing 0.00001 g. of copper per cc. from a pipette graduated in tenths cc. until an equivalent color is produced.

Calculations:

$$\frac{(\text{cc. of standard}) \times (\text{g. of Cu per cc.}) \times 3}{\text{wt. of sample}} \times 100 = \%\ \text{Cu}$$

Notes

(1) The bromine is added to precipitate the manganese as manganic hydroxide, since manganous hydroxide is soluble in ammonium salts. Since as much as 0.000075 g. of manganese has no effect on the indicator, the bromine treatment may be omitted if the amount of manganese in the rubber is known to be less than 0.001%.

(2) The standard copper solution is a solution of copper sulfate ($CuSO_4$) in a 5% NH_4OH, the strength of which is 0.00001 g. of Cu per cc. of solution. It is standardized by electrolysis, using platinum electrodes.

Latex

The Committee prepared a manuscript entitled "Specifications for Testing the Variability of Normal and Concentrated Latex." This manuscript was sent

to the various latex companies in the United States for criticism. The various criticisms were taken under advisement by the Committee in New York. Following the meeting in New York, the manuscript was revised and copies were sent for criticism to various latex companies in this country and to various technical organizations and individuals in Europe and the Far East. As soon as the revised manuscript has been criticized, it will be rewritten, and it is hoped that it will then be ready for publication.

Light and Dark Smoked Sheet

The Committee has previously reported that it was unable to verify the reports from Europe that light colored smoked sheet tends to be harder and more difficult to break down than dark colored smoked sheet.

Samples of light and dark sheet sent from the Far East were again checked for plasticity and were found to be substantially the same. The rates of vulcanization of the samples were also found to be the same. This information has been reported to the Rubber Research Institute.

Plasticity

Work on plasticity has been continued during the past six months, but the Committee is not yet in a position to make any definite recommendations. Work on this problem is being continued.

Coagulating Agents

In the *Rubber Research Institute of Malaya Bulletin,* Vol. 7, No. 1, June, 1936, Edgar Rhodes reports on "A Survey of Latex Coagulants Used by Malayan Smallholders." Following the publication of this report and other information available, the Crude Rubber Committee wrote to the various producing organizations in the Far East, suggesting that some effort be made to assure that specified coagulants were used and that bales of rubber so prepared be identified so that the consumer would know that the rubber under consideration was prepared according to definite specifications, as far as coagulating agents are concerned. It is of interest to report that Edgar Rhodes found that sulfuric acid was employed to a much greater extent than had previously been supposed. Most of the holders, however, employed formic and acetic acids. Hydrochloric acid and, to a lesser extent alum, were also used as coagulating agents.

The Committee has received a very enthusiastic letter from O. de Vries, who states that he is very definitely of the opinion that such a procedure would be of material assistance in the standardization of crude rubber.

Aging

A series of test recipes and methods have been investigated by means of 25 samples each of No. 1-X smoked sheet and prime Chinese sheet for the purpose of establishing recipes and testing methods for determining the variability in the aging characteristics of crude rubber. Despite the mass of information available, the Committee considers it advisable at this time to defer presentation of the data or recommendations.

Cleanness

The Committee again wishes to urge that the entire industry insist on receiving a uniformly clean product.

The Committee has received a fairly large number of reports from various technical organizations in Europe and the Far East. These reports have all

been of considerable interest and have helped the Committee members in the understanding of the problems confronting the producers. The Committee has commented on several of the papers in communications sent to the originators. In most cases, however, these reports have not required replies.

The Committee is particularly pleased to report that three national research organizations are being set up, *viz.*, in France, Holland and England, for the purpose of investigating fundamental problems connected with rubber and technical problems relating to the investigation and development of existing and new uses of rubber. Their investigations will be coördinated by an international rubber research board.

The Committee again wishes to express its appreciation to the various individuals and organizations on the producing side of the crude rubber industry who have been coöperating with the Committee in its work.

REPORT V

PREPARED FOR THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY IN ROCHESTER, N. Y., SEPTEMBER 6, 1937

Committee: E. B. Babcock, L. M. Freeman, R. H. Gerke (Chairman), G. A. Sackett, J. C. Walton

The Crude Rubber Committee met in Akron, Ohio, June 4, 1937, at which time Harold Gray announced his resignation from the Crude Rubber Committee. H. L. Trumbull appointed R. H. Gerke Chairman and L. M. Freeman, The B. F. Goodrich Company, to replace Harold Gray.

The Committee regrets to hear that Mr. Gray can no longer serve with them, and desires to congratulate him on his successful leadership.

At this meeting the final draft of the "Specifications for Testing the Variability of Normal and Concentrated Latex" was approved for distribution to the list of correspondents for further comment and criticism before final approval, which was planned for 1938. The Committee hereby desires to officially thank all those who kindly offered their services in coöperating in the preparation of the latex specifications.

W. T. L. ten Broock, of the Goodyear Rubber Plantations, was present and stated that the establishment of the standard recipe was a big advance. He also described the work of the Crude Rubber Committee in the Dutch East Indies. In connection with the standard recipe, work is in progress in the Far East in the evaluation of the Schopper machine *vs.* the Scott machine, which has been used in this country for the puprose of testing rubber cured according to the recipe.

Three unfinished projects of the Crude Rubber Committee consist of a method for testing cleanness, a method for preparing crude rubber samples for the plasticity determination, and a recipe which will be satisfactory for testing rubber with respect to variability of aging. While some data have been obtained on these subjects, it appears that these projects are of such a complex nature that it will be some time before satisfactory solutions can be reached.

The Committee has received correspondence from Professor Charles Dufraisse for the many kindnesses extended, especially by Mr. Gray, in arranging an itinerary for Mr. Jean LeBras, and also by many other members of The Division of Rubber Chemistry who have coöperated in entertaining Mr. LeBras in their plants and laboratories.

REPORT VI

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY IN DETROIT, MICHIGAN, MARCH 28, 1938

Committee: E. B. Babcock, L. M. Freeman, R. H. Gerke (Chairman), G. A. Sackett, J. C. Walton

The Crude Rubber Committee is now engaged in the development of a procedure for the quantitative determination of dirt in rubber. The variability of plasticity has received considerable attention. The essental problem in this project is the development of a standard method of preparation of a sample from a bale of rubber.

At this meeting, Tentative Procedures L1 to L13 for Testing the Variability of Normal and Concentrated Latex were developed and will be published.

The Committee is receiving whole-hearted coöperation from producers' organizations. In this connection, a letter from Prof. Charles Dufraisse of the Institut Français du Caoutchouc has been acknowledged. Also, a letter from H. J. Page, Director of the Rubber Research Institute of Malaya, who has asked six searching questions, which constitute a very excellent starting point for the development of specifications for uniform smoked sheet. These questions will be brought to the attention of the members of The Division of Rubber Chemistry for thorough discussion.

After reading the report, the Chairman raised before The Division, for open discussion, the question whether consumer requirements vary and whether or not it is desirable for all rubber to be of one standard quality. The net result of a long and spirited discussion was that it would be acceptable to have clean rubber of one standard quality and always uniform in chemical and physical properties. There was some preference for light color. There was no apparent demand for sheet rubber of different standard qualities. Off-grades were excluded from the discussion.

REPORT VII

PRESENTED AT THE MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, BALTIMORE, MARYLAND, APRIL 5, 1939

Committee: E. B. Babcock, L. M. Freeman, R. H. Gerke (Chairman), Ian Patterson for G. A. Sackett, J. C. Walton, W. S. Davey (Guest)

Final revision of the Tentative Procedures for Testing the Variability of Normal and Concentrated Latex has been completed. Publication is being arranged. The Committee wishes to thank especially the foreign correspondents for their helpful suggestions.

The reports of the Crude Rubber Committee have been condensed and collected together for publication.

The procedure for quantitative dirt, which depends on dissolution of the rubber and filtration through a 200-mesh sieve, is being developed.

The problem of preparation of samples from bales for the plasticity determination is still unsettled. Further examination of European and U. S. procedures of preparation of samples will be carried out, with the object of selecting one which is adequate. In contrast, most of the sampling of crude rubber in production is from masticated blends. Obviously this is a much simpler problem than sampling from bales.

Progress has been made on the development of an apparatus for determining the mechanical stability of latex. .

With reference to the London Advisory Committee for Rubber Research, Tentative Standards for Raw Rubber (minutes of Sub-Committee on Standardization of Raw Rubber, November 18, 1938, Section D), which is given below, the Crude Rubber Committee is in agreement with the principles of setting limits for the standardization of rubber, and believes that the London Advisory Committee's efforts in this direction are to be commended.

Tentative Standard Figures for Vulcanization of Plantation Rubber

MIXTURE A

Rubber	100
Sulfur	10

(1) Vulcanization to a good "technical cure" should be obtainable with a vulcanization period of not less than 70 minutes and not more than 100 minutes at 148°C.

(2) The tensile strength at this "technical cure" should be not less than 130 kg. per sq. cm.

Note.—A period of 24 hours at ordinary temperature (15-30° C.) should elapse between mixing and vulcanization, and a further period of 24 hours at 28° C. between vulcanization and testing at 28° C. These periods of rest should be observed, both for mixings A and B, and the mixed and vulcanized rubber should be protected from light.

MIXTURE B

Rubber	100
Sulfur	3.5
Zinc oxide	6
Stearic acid	0.5
Mercaptobenzothiazole	0.5

(1) A good "technical cure" should be attained with a vulcanization period of not less than 30 minutes and not more than 60 minutes at 125°C.

(2) The tensile strength of this vulcanized rubber should be not less than 130 kg. per sq. cm.

(3) The load necessary to produce an elongation of 700%, *i.e.*, to stretch a length of 1 inch to 8 inches, of this vulcanized rubber should be not less than 60 kg. per sq. cm. nor greater than 130 kg. per sq. cm.

Note.—A desirable refinement of this test for qualifying the standard rate of curing of rubber (smoked sheet or crepe) would be to grade as best medium rate of curing when the load at 700% is not less than 85 kg. per sq. cm. nor greater than 120 kg. per sq. cm.

(4) A cylindrical test-piece of unvulcanized mixture B, 1 cm. in height and 1 cm. in diameter, is kept at 95°C. for 30 minutes and a load of 600 grams is then applied at the same temperature for 30 seconds, after which the load is released. The vertical recovery in the height of the specimen during the first 30 seconds after release of the load shall not be greater than 30% of the extent of the vertical deformation immediately before release of the load.

We prefer the limits to set up in the note to paragraph 3.

With respect to plasticity in Paragraph (4), we question the use of an unvulcanized mixture for the determination of the plasticity of crude rubber.

THE CRUDE RUBBER COMMITTEE:
E. B. BABCOCK,
L. M. FREEMAN,
G. A. SACKETT,
J. C. WALTON,
R. H. GERKE, *Chairman.*

VARIATION IN THE COMPOSITION AND PROPERTIES OF FRESH LATEX

AND SUBSEQUENT CHANGES ON AMMONIATION *

EDGAR RHODES

RUBBER RESEARCH INSTITUTE OF MALAYA, KUALA LUMPUR

INTRODUCTION

This paper describes results which have been obtained on latex from a small area of old seedling rubber, close to the Rubber Research Institute and under close supervision by it, over a period of fourteen months from the time of opening after having been out of tapping for some years. It represents an attempt to follow some of the changes in composition and properties of latex, which are of special interest to those concerned more with preserved and concentrated latex as an article of commerce than variations in the properties of crude rubber. For this reason changes in dry rubber content, total solids, acetone extract and acid value of whole latex film, surface tension, viscosity and stability have all been followed, both in the fresh latex and preserved latex made from it.

EXPERIMENTAL

The latex used in the experiments came from a single tapper's task in a four acre block of rubber trees situated within fifty yards of the Rubber Research Institute. The trees were brought into alternate daily continuous tapping on April 1, 1937, after having been in rest for some years, and latex was examined regularly from that date until the end of May, 1938. Because the area is so close to the laboratories, supervision is easy and the fresh latex can be brought in for examination much more quickly and much earlier than on the normal rubber estate. The possibilities of error, due to changes caused by incipient putrefaction in the field, are thus reduced to a minimum.

In the course of the fourteen months' period, 163 samples of latex were drawn for examination from the alternate daily tappings. This represents nearly three samples per week.

When each sample was drawn, it was divided into two parts. The one part was examined immediately in the unammoniated condition; the other part was ammoniated immediately to 0.7% ammonia (with a 25% solution of ammonia in water), and on this ammoniated part, some tests were made immediately, and others after storage periods of 10 days and 50 days, respectively.

The procedure for the various tests was as follows:

Dry Rubber Content.—Determined by acid coagulation of a known weight of latex (about 20 g.). The coagulum is rolled thin with ample washing during rolling, dried at 70° C. and weighed.

Total Solids.—A known weight of latex (about 10 g.) is evaporated to dryness at 70° C. in a shallow-weighed vessel and the weight of dry solids determined.

Acetone Extract.—About 30 cc. of latex, whether fresh or ammoniated, are spread very thinly on a glass frame (21 in. square). Air is blown over the film

* Reprinted from the *India-Rubber Journal*, Vol. 97, No. 3, pages 82-88, January 21, 1939. Two tables are omitted.

by an electric fan. After two hours the dried whole-latex rubber is removed, cut into small pellets and stored overnight in a desiccator. Five grams of the whole latex rubber are then extracted for eight hours with acetone. The weight of acetone-soluble matter is determined after removal of the solvent.

Acid Number.—The whole extract from each sample is dissolved in 20 cc. alcohol (95%), and titrated with 0.01*N* alkali against phenolphthalein as indicator. The acid valve is expressed as the number of mg. KOH required to neutralize the extract from 100 g. whole-latex rubber.

Surface Tension.—Determined with a Du Nüoy tensiometer of the direct reading type. Surface skimming is avoided by placing the vessel containing the latex inside a deeper dish, and covering this loosely with two flat pieces of glass, which leave only sufficient opening to admit the wire carrying the loop.

Viscosity.—Determined with a Höppler viscometer at 30° C.

Stirring Stability.—Determined with the slow-speed apparatus devised by the London Advisory Committee for Rubber Research. Latex is diluted to a dry rubber content of 30%, and after adjusting the ammonia content to 0.7%, 600 cc. are stirred at 600 r.p.m. in presence of 162 g. zinc oxide (90% calculated on dry rubber), which is blown in dry during the first 30 seconds of stirring. Stirring proceeds to the "viscosity end point" described by Rhodes (Annual Rept. Rubber Research Inst. Malaya, **1936**, p. 102).

Ease of Creaming.—200 cc. latex are mixed with 14 cc. of 3% Tragon A solution (0.2% Tragon A on the latex) and left for creaming. After a period of 48 hours the serum is removed, and the dry rubber content of the cream is determined. This dry rubber content is taken as the index of "ease of creaming".

It will be observed that stirring stability tests were not made on the freshly ammoniated latex. The reason is that because of the slowness of the stirring and the very high results always given by very fresh latex, it was not possible to complete a test in a working day.

The individual alternate daily records are not given in this paper because of their bulk. Instead, the monthly means for the various properties are shown in Figures 1 to 8, inclusive.

Table I gives correlation coefficients for various pairs of properties. These were calculated from the actual individual day-to-day records, and not from the monthly means.

DISCUSSION

General Observations

Dry Rubber Content and Total Solids.—It will be seen from Figures 1 and 8 that after the first three months when the trees had reached full flow, the dry rubber content of the fresh latex was generally low in the wet months, and *vice versa*. This is as might have been expected.

Too much significance may not be attached to the fact that the values for dry rubber content after 10 days' storage are invariably lower than those for the fresh latex, because the difference must be due mainly to the dilution caused by the initial ammoniation with 25% aqueous ammonia.

There is one feature worthy of note which arises from an examination of the monthly means for total solids and dry rubber content of the fresh and the preserved samples. In the case of the fresh latex, the difference between total solids and dry rubber content varied from month to month between the limits of 2.3 and 2.7%, whereas in the case of the ammoniated latex the month-to-month

TABLE I

Correlation of Properties

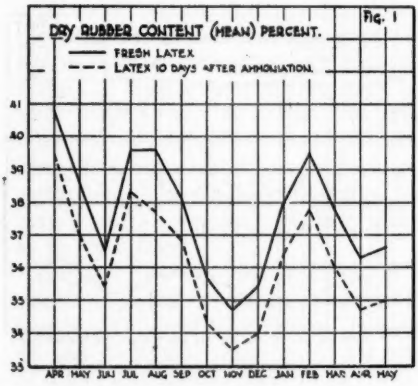
Property	Correlated with	No. of Pairs	Coefficient of Correlation	Significance* (SS, S, or —)
D.R.C. Fresh latex	(i) Acid number. Fresh latex	135	−.282	SS
	(ii) Acetone extract. Fresh latex	135	−.390	SS
	(iii) Ease of creaming. Fresh latex	127	.394	SS
	(iv) Viscosity. Fresh latex	82	.263	S
	(v) Stirring stability after 10 days' storage	134	−.369	SS
D.R.C. After 10 days' storage	(i) Acid number after 10 days' storage	151	−.169	S
	(ii) Acetone extract after 10 days' storage	151	−.340	SS
	(iii) Viscosity after 10 days' storage	122	.863	SS
Acetone extract. Fresh latex	(i) Acid number. Fresh latex	146	.598	SS
	(ii) Ease of creaming. Fresh latex	136	−.170	S
	(iii) Surface tension. Fresh latex	93	−.037	—
Acetone extract after 10 days' storage	(i) Acid number after 10 days' storage	156	.284	SS
	(ii) Surface tension after 10 days' storage	129	−.012	—
Acetone extract after 50 days' storage	(i) Acid number after 50 days' storage	159	.408	SS
	(ii) Surface tension after 50 days' storage	113	.129	—
Acid number. Fresh latex	(i) Surface tension. Fresh latex	93	−.043	—
	(ii) Ease of creaming. Fresh latex	136	−.0515	—
Acid number. After 10 days' storage	(i) Surface tension after 10 days' storage	129	−.324	SS
Acid number. After 50 days' storage	(i) Surface tension after 50 days' storage	113	−.135	—
Stirring stability. After 10 days' storage	(i) Acetone extract after 10 days' storage	155	.245	SS
	(ii) Acid number after 10 days' storage	155	.294	SS
Stirring stability. After 50 days' storage	(i) Acetone extract after 50 days' storage	158	−.110	—
	(ii) Acid number after 50 days' storage	158	−.242	SS

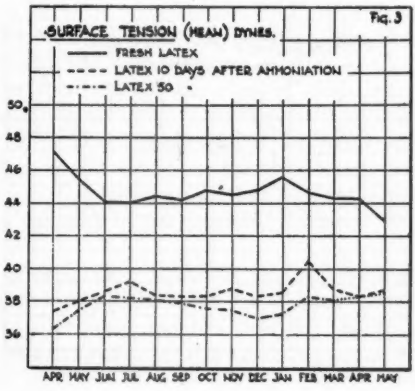
* SS = P < .01. Usually taken as highly significant.
S = P < .05. Usually taken as significant because there is between 1%-5% chance of the result having occurred by chance.
— = P > .05. Usually taken as not significant.

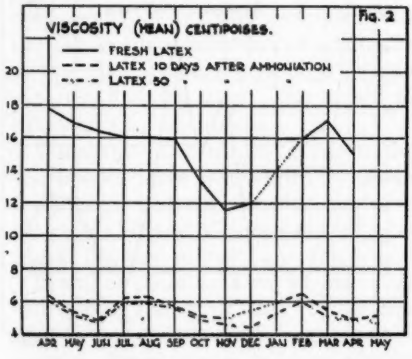
differences were invariably higher, and lay between the limits of 2.8 and 3.1%. It would appear therefore that ammonia has reacted with some part of the total solids in such a way as to render it non-precipitable by acid on coagulation for the determination of "dry rubber content."

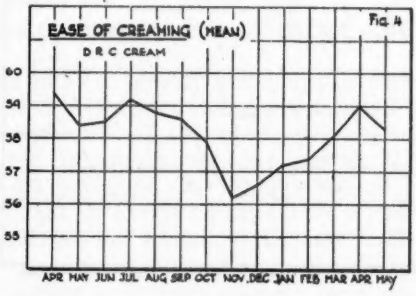
Acetone Extract and Acid Number.—It will be seen from Figures 6 and 7 that ammoniation produces striking changes in the amount of acetone-soluble substances in the whole-latex rubber, and also in the acidity of the acetone-soluble matter.

During every month the acetone extract was greater after 10 days ammoniation







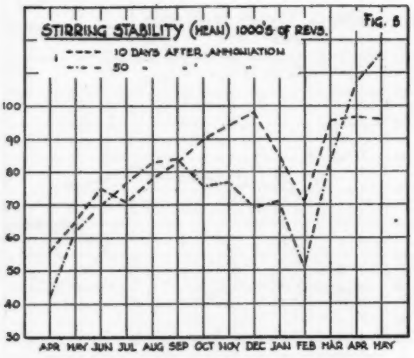


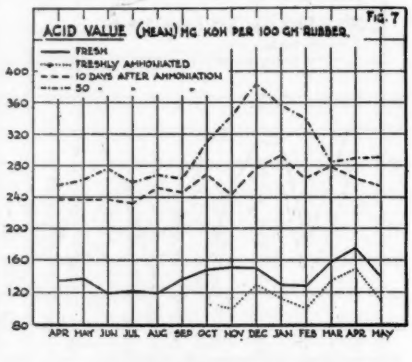
than when fresh. In most months there was a slight further increase between 10 and 50 days.

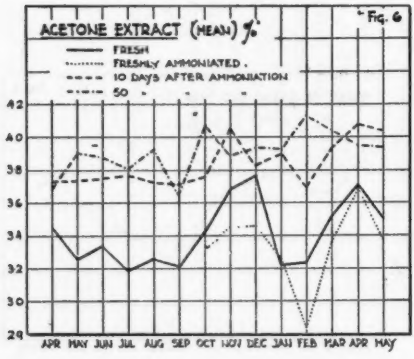
In the case of the acid number, the differences were still more striking. After 10 days' ammoniation, the acid number of the acetone extract was approximately double that of the fresh latex, and further increases appear invariably to occur between 10 and 50 days. In some months these further increases were very large.

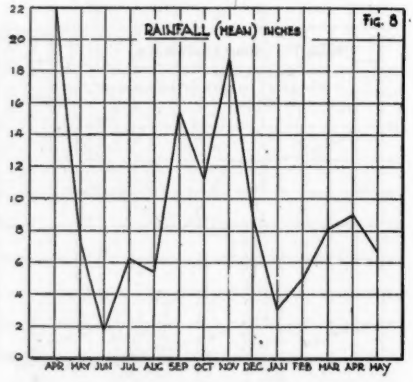
A further interesting feature is provided by the values for acetone extracts and acid values for whole rubber prepared from latex immediately after ammoniation on the day of collection. It would be expected that the figures for such rubbers would be indistinguishable from those for the fresh unammoniated latex. This is not however the case. Figures 6 and 7 give the monthly means

for freshly-ammoniated latex for eight months, and it will be seen that during six of those months, the acetone extract means for fresh latex were the higher, while during only two months were they virtually the same as those for the freshly-ammoniated material. More marked differences are shown by the eight monthly means for the acid numbers of the acetone extract from fresh and freshly-ammoniated material. Here it is seen that the acid number of whole rubber from freshly-ammoniated latex was invariably less than that from fresh latex rubber. The only explanation of this unexpected finding which can be advanced at present is that "fresh" latex usually contains, besides the normal









acetone solubles, a certain small amount of adventitious acetone-soluble acid produced by the action of bacteria between tapping and collection, and that the addition of ammonia produces from the bacterial acid a salt which is insoluble in acetone. This would account for the lower acetone extract and acid number of freshly-ammoniated latex, but it is emphasized that there is at present no practical proof of the correctness of such a hypothesis.

These values for the changes in acetone extract and acid number of whole-latex rubber from fresh, freshly-ammoniated and stored latex are quite the most worthy of note of any in this paper. They indicate first a reduction in acetone extract and acid number on addition of ammonia, followed by a progressive hydrolysis presumably by ammonia, which is usually well-advanced in

ten days and thereafter proceeds more slowly. It is not possible to deduce from the available figures whether or not the changes are complete in fifty days, but it seems probable that they are very nearly so. The results demonstrate a tangible difference between the composition of freshly ammoniated latex and the preserved latex of commerce.

The view is commonly held that the acid number of whole latex rubber is due to free fat acids and other acids but that, in ammoniated latex, these acids are present as ammonium soaps and salts. If this view is correct, then these ammonium soaps, etc., must decompose again to free acids, either during the drying of the latex film at room temperature or during the process of acetone extraction; otherwise it is difficult to see in what manner the acid number of the acetone extract of whole-latex rubber could double itself during the first ten days after preservation. The fact that the acid number of the acetone extract of freshly ammoniated latex is less than that of the original fresh latex, lends color to the view that the ammonia might have formed some soaps or salts and so reduced the acid value, but these lower results could obviously not have been obtained if decomposition had occurred again during drying and extraction. The evidence therefore leads to the speculation that the fat acids may perhaps be present as such, and not as soaps in ammoniated latex, as well as in fresh latex.

Surface Tension.—From Figure 3 it is seen that ammoniation and storage results in a fall in surface tension. The monthly means for fresh latex varied between 47.2 and 42.9 dynes. During 10 of the 14 months they lay between 44 and 45 dynes. The means for ammoniated latex 10 days old lay between 37.4 and 40.5 dynes, while those for latex 50 days old were always very slightly lower, *viz.*, 36.3 and 38.6 dynes.

Observations for which experimental figures are not presented here show that the fall in surface tension on ammoniation is not immediate as, say, in the case of viscosity. It progresses steadily at a rate of less than one dyne per 24 hours over the first ten days. This would indicate a gradual release of surface active substances by hydrolysis.

Viscosity.—The values in Figure 2 illustrate the already well-known changes which take place when latex is ammoniated. Whereas the viscosity means for fresh latex between the dry rubber contents of 34.7 and 40.8% show values between 11.6 and 17.8 centipoises, those for the ammoniated latex between 33.5 and 39.5% dry rubber lie in the zone 4.8-6.5 centipoises after 10 days' storage.

It will be observed from Figures 1 and 2 that the curves for dry rubber content and viscosity after 10 days' storage show maxima and minima in the same places. This is not strictly true in the case of viscosity of fresh latex *vs.* dry rubber content. Fresh latex is however so prone to show exaggerated viscosity variations, due perhaps chiefly to incipient coalescence caused by bacterial infection, that this is not surprising.

Stirring Stability.—Figure 5 indicates that during nine of the fourteen months the mean values for stability, measured by this unusual technique, indicate a fall during the 10-50 days' storage period, while during the other five months the reverse was the case. For this anomalous behavior no explanation suggests itself.

From Figures 1 and 5 however, there would appear to be some connection between dry rubber content and stirring stability after ten days' storage, since the two relevant graphs are similar but reversed, showing maxima against minima, and *vice versa*, as if a rather low initial dry rubber content might connote a relatively high stability.

Ease of Creaming.—If one omits from consideration the mean values for the months March to May, 1938, inclusive, Figures 1 and 4 would seem to indicate a connection between dry rubber content and ease of creaming.

Correlation of Properties with One Another

In comparing various sets of means and in examining Figures 1 to 8, sundry points of similarity have been seen. However, to avoid faulty generalizations, Table I was prepared: this gives correlations of the actual day-to-day results for various pairs of properties, and enables one to form more accurate conclusions as to the dependence or otherwise of one factor on another. The relevant correlations are discussed below:

Dry Rubber Content with Acetone Extract, and with Acid Number.—From Table I the dry rubber content of fresh latex gives significant negative correlations with both the acetone extract and the acid number of whole-latex rubber from such latex. The results are derived from 135 samples of latex, and whole rubber therefrom. Similarly, the correlations for dry rubber content in 10 days' old latex with the acetone extract and acid number are also negative and significant. Here the results are derived from 151 latex samples and rubbers. In no case, however, are the correlation coefficients very high, but it seems fairly safe to argue that low acetone extracts and acid numbers are to be suspected in the whole-latex rubbers from rubber-rich natural latices. If Figure 1 is reversed, it shows maxima and minima in approximately the same places as the relevant parts of Figures 6 and 7.

Acetone Extract with Acid Number.—There is positive and significant correlation between these two characters in the case of fresh latex, and also in latex stored for 10 and 50 days, respectively. Since however the acetone extract itself contains the acids from which the acid number is derived, it is dangerous to draw conclusions from this data. The correlation may have no more meaning than that of the population of a town with the number of cases of whooping cough. It can, however, be said that high acid numbers are likely to be found when acetone extracts are high.

Surface Tension with Acetone Extract and with Acid Numbers.—The data in Table I show no significant correlation between the surface tension of fresh latex, and either the acetone extract or the acid number of the whole-latex rubber from it. In latex stored for 10 days there appears to be a negative and significant correlation between surface tension and acid number, but there is no correlation with acetone extract. After 50 days' storage no significant correlation is shown either with acetone extract or acid number.

It seems therefore that, although the acids present in the acetone extract may at some stages during storage play some part in causing the fall in surface tension, this provides no evidence that changes in the acetone extract and its acid number are the major factor in bringing about surface tension changes.

Viscosity with Dry Rubber Content.—Table 3 shows that the degree of correlation between the dry rubber content and the viscosity of fresh latex is not very high, whereas that between the dry rubber content and viscosity of the same latices after ammoniation and storage for 10 days is positive, significant and very high, *viz.*, the order of 0.86.

This high value leaves no doubt that dry rubber content is the controlling factor in the viscosity of the preserved latex. It also adds weight to the view that one of the effects of ammonia on fresh latex is to disperse incipient aggregations which occur in fresh latex between tapping and collection, and which are

responsible for the irregular viscosity values and consequent poor correlation with dry rubber content.

Stirring Stability with Dry Rubber Content, and with Acetone Extract and Acid Number.—It is seen from Table I that the initial dry rubber content is negatively and significantly correlated with the stirring stability after 10 days' storage. This implies that a low initial dry rubber content usually connotes a rather high stability during the early stages of storage. Since under the present conditions of test all latex samples are diluted to the same dry rubber content (30%) before testing, this would suggest that substances accessory to the rubber may play an important part in determining early stability. It has already been noted that acetone extract and acid number are correlated negatively with dry rubber content, and this leads to the possibility that the acetone exract or its acid number might be positively and significantly correlated with stirring stability. Examination of the data for acetone extract and acid number after 10 days' storage, with stability after 10 days' storage, shows that these characteristics are so correlated, but the coefficient of correlation is not very high. If now stability at 50 days' storage is set against acetone extracts and acid numbers for the same storage period, no correlation is found with acetone extract, and a significant and negative one with acid number.

It is clear therefore that the available data do not provide an explanation of the changes in stability which occur on ammoniation and storage. The data indicate that low initial dry rubber content may tend to promote higher earlier stability, but there is no evidence that either it or the acetone extract and acid number are major factors in determining initial stability or subsequent changes in it.

Ease of Creaming with Dry Rubber Content, with Acetone Extract and with Acid Number.—The data in Table I show a positive and significant correlation between the initial dry rubber content of latex and its ease of creaming with Tragon-A. Negative correlation also occurs with the acetone extract and the acid number of the fresh latex, but in the first case the correlation is not highly significant, and in the second it is without significance.

It is obvious therefore that, although high initial dry rubber content may be a favorable factor in creaming, there are other factors probably more important which the present data are inadequate to disclose.

SUMMARY

Systematic examination has been made of 163 samples of latex drawn at the approximate rate of three per week over a period of fourteen months from a single tapper's task on old seedling trees, newly opened after several years' rest on the continuous alternate daily system. The latex samples were all examined, both in the fresh condition and after 10 days and 15 days preservation with 0.7% ammonia; during the last eight months certain tests were also made on the latex immediately after ammoniation on the day of collection.

The tests included dry rubber content, total solids, acetone extract and acid number of whole-latex rubber films, surface tension, viscosity, stirring stability and ease of creaming.

It has been observed that:

(1) The difference between percentage total solids and percentage dry rubber content is greater after 10 days' preservation than in the fresh condition.

(2) The acetone extract and its acid number from whole-latex film are less in freshly-ammoniated latex than in fresh latex, and very much greater in

ammoniated latex stored for 10 days. The acid number after 10 days preservation is usually about twice that of the fresh latex. These findings and their implications are discussed in the text, in which experimental figures are given. High dry rubber content usually connotes low acetone extract and acid value in the fresh latex.

(3) Values for surface tension before and after ammoniation are given. The fall in surface tension as a result of ammoniation has not been proven to be governed by the changes in acetone-soluble material, or the acid number thereof.

(4) The viscosity of ammoniated latex is shown to be very significantly correlated with its dry rubber content. In the case of fresh latex the degree of correlation is much less; a possible reason for this is advanced. Experimental results are given.

(5) The initial stirring stability is shown to be influenced by the initial dry rubber content of the latex. The data do not provide an adequate explanation of the changes in stability which take place on storage.

(6) The creaming ease of new latex appears also to be influenced by its initial dry rubber content, but the present data are not adequate fully to explain the variations which are noted.

ACKNOWLEDGMENTS

The author is much indebted to H. Fairfield Smith, statistician at the Rubber Research Institute, for the various correlations of properties and to K. C. Sekar, T. Sivvakalundoo Nathan and Che Abdul Wahid bin Abdul Wahab for much help in the experimental work involved.

THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX *

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PART I. RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY

INTRODUCTION

Data on the viscosity of preserved and concentrated latex are meagre, and in most cases results have not been reported in absolute values. No satisfactory mathematical relationship between the dry rubber content and the absolute viscosity of latex and concentrates appears to have been developed, although Bächle (Rubber Chem. Tech. **10**, 675 (1937)) reports agreement between results obtained on latex up to a dry rubber content of 45%, and the formula of Guth for suspensions of spheres. In the present work a very large number of observations on preserved field latex, centrifugal concentrates, and filtration concentrates have been made, and from them mathematical expressions have been derived which express with reasonable accuracy the viscosity of preserved latex and concentrates within the range of 0-68% dry rubber.

EXPERIMENTAL

PRESERVED FIELD LATEX

It is well known that different samples of preserved field latex of identical dry rubber content do not necessarily have identical viscosities. Differences are noted from source to source, and from time to time at the same source. It was sought to smooth out these variations and obtain values for what might be termed average preserved latices by making a large number of determinations on latex from different sources chosen to cover the widest possible dry rubber content range for natural latex. Altogether 950 samples of natural latex were collected and tested after having been ammoniated to an ammonia content of 0.5%. The samples were collected as opportunity offered over a period of approximately six months from about twelve different sources, of which one, Kepong Estate, Selangor, predominated. The latices of low, dry rubber content (26-32%) were of necessity obtained mainly from a single area of rubber which was being subjected to a mild form of "slaughter tapping" prior to replanting, while the rich latices (D.R.C. 44-52%) came from a different area of the same estate during the first few days of normal tapping after rest.

Dry rubber content and viscosity determinations were carried out in duplicate on each sample. The first 533 samples were tested for viscosity in a simple pipette viscometer, which had been previously calibrated with standard solutions of cane sugar. The 417 samples collected subsequently were tested by means of a Höppler viscometer. All tests were carried out at a temperature of 30° C. The detailed results on the individual samples, together with the records of the source of each sample, were destroyed by fire at the Institute, but fortunately,

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summary sheets which happened to be in the author's hands at the time escaped. In making the summaries the results had been grouped into classes of 2% dry rubber content, and the mean D.R.C. and mean viscosity had been calculated for each class. No other information remains.

The viscosity results obtained by the two methods are in good agreement, and the results obtained by both methods have therefore been combined in Table I.

TABLE I

PRESERVED FIELD LATEX

Combined Viscosity Results by Pipette and Höppler Apparatus

D.R.C. Group	Number of samples in Group	Mean D.R.C. (found)	Mean n (found) (centipoises)	n Calculated (centipoises) from: $\log n = 0.034 + 0.952 \tan p$
>26—28	26	27.4	3.2	3.4
>28—30	151	29.3	3.7	3.7
>30—32	150	31.0	4.1	4.0
>32—34	113	33.1	4.8	4.5
>34—36	97	35.1	5.5	5.0
>36—38	103	37.0	5.8	5.6
>38—40	112	39.1	6.4	6.4
>40—42	120	40.8	7.2	7.2
>42—44	37	42.8	8.5	8.2
>44—46	15	45.1	9.8	9.8
>46—48	11	47.0	11.9	11.3
>48—50	12	49.0	13.7	13.4
>50—52	3	50.3	15.4	15.1
Total	950			

CENTRIFUGAL CONCENTRATES

Seventy-three samples of centrifugal concentrates were made available to us by the courtesy of Dunlop Plantations, Ltd. These were prepared to cover a dry rubber content range of approximately 56-63%. They were tested by the pipette method, under conditions similar to those for normal preserved latex. Here again details of the individual tests were lost by fire, but a summary showing the mean dry rubber content and mean viscosity by groups of 1% D.R.C. escaped destruction, and forms the experimental part of Table II.

TABLE II

VISCOSITY OF CENTRIFUGAL CONCENTRATES

D.R.C. Group	Number in Group	Mean D.R.C. (found)	Mean n (found) (centipoises)	n Calculated (centipoises) from: $\log (n+0.309) = 0.143 + 1.0139r$
>56—57	3	56.6	27.7	28.9
>57—58	3	57.8	31.8	33.7
>58—59	10	58.6	38.1	37.5
>59—60	21	59.6	40.5	43.1
>60—61	31	60.4	45.1	48.7
>61—62	4	61.3	48.5	55.8
>62—63	1	62.9	57.5	72.3
Total	73			

Concentrate-serum Mixtures and Concentrate-skim Mixtures

Determinations in the range provided by natural preserved latex and centrifugal concentrates do not give a complete picture of the relationship between dry rubber content and viscosity and, to obtain more complete pictures, recourse was had to the preparation of concentrate-serum and concentrate-skim mixtures. Two procedures were used. In the first, preserved field latex was filtered in a number of Leclanché cells, themselves placed in damp chambers to avoid evaporation concentration of the filtered serum. The filtered serum and the filtration concentrate were collected and these, together with the original unconcentrated latex, provided a means of producing mixtures covering the whole range of 0-68% dry rubber. Mixtures of the original latex with varying amounts of its concentrate were used for the high zone determinations, and similar mixtures of latex with its own filtered serum were used for the lower zone. For experimental purposes, concentrate-latex-serum mixtures were prepared for test from three different lots of latex. Two of the lots (Series 1 and Series 2) came from the same estate on different days, and the third (Series 3) came from a different estate.

In the second procedure a batch of latex drawn from the same estate as Series 1 and 2 was centrifuged, and the centrifugal concentrate and skim so produced were used in preparing skim-cream mixtures covering the range 10-60% dry rubber for test.

The three series of filtration concentrate-serum mixtures (Series 1, 2 and 3) were tested in the Höppler instrument. The centrifugal concentrate-skim mixtures were tested earlier by the pipette method. It was not to be expected that the four series would give identical curves for the viscosity dry rubber content relationship, because each series was derived from a different parent latex sample.

That from which Series 3 was produced came from an estate which invariably gives a more viscous latex than that which provided the parent latices for the other three series. It was expected, however, that the four sets of results, although not identical, would be similar. This proved to be the case, Series 3 showing higher results throughout than the other three series.

DISCUSSION

With the data contained in Figures 1, 2 and 3, it has been possible to test the applicability of several theoretical formulas which have been put forward from time to time for the viscosity of emulsions and suspensions.

It will be observed at once from the data that the dry rubber content-viscosity relationship cannot be expressed by a straight line. The expression:

$$n=n_0(1+2.5v/V)$$

due to Einstein could therefore be ruled out at once, because it is a straight line relationship which was only intended, in the first place, for low concentrations (*i.e.*, low values of v/V, where v and V represent the volumes of the dispersed phase, and that of the dispersion respectively).

The extended expression:

$$n=n_0(1+2.5v/V+7.8(v/V)^2)$$

used by Bächle is, as he points out, similarly inapplicable, except over a limited range.

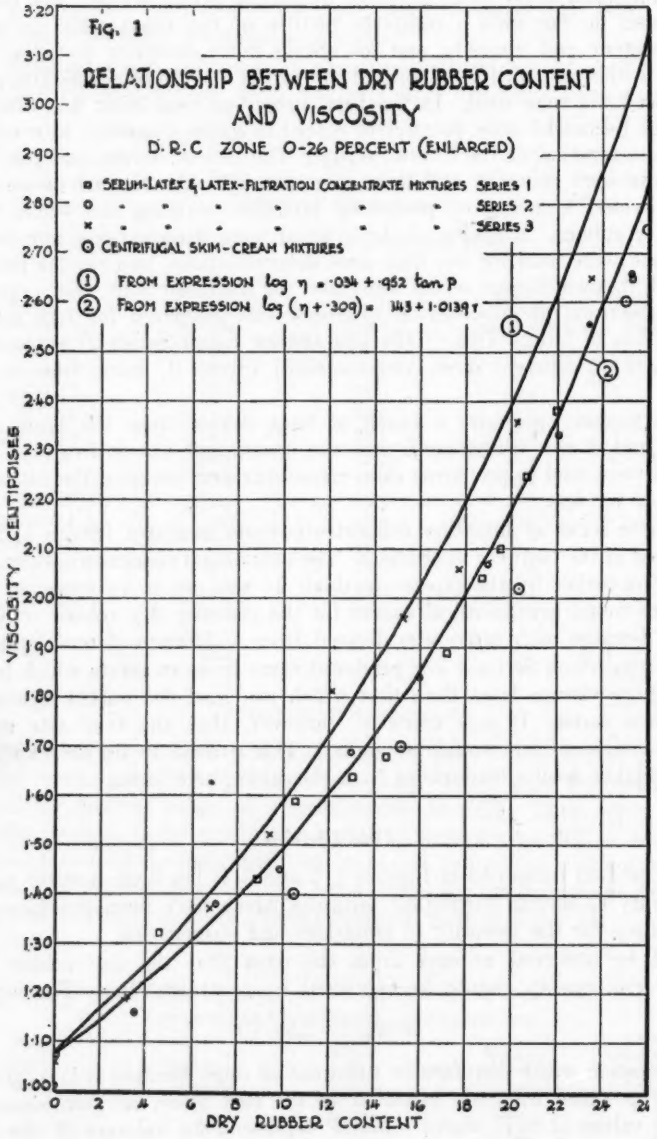
Fig. 1
RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY
D·R·C ZONE 0-26 PERCENT (ENLARGED)
SERUM-LATEX & LATEX-FILTRATION CONCENTRATE MIXTURES SERIES 1
SERIES 2
SERIES 3
CENTRIFUGAL SKIM-CREAM MIXTURES
1 FROM EXPRESSION log η = ·034 + ·952 tan P
2 FROM EXPRESSION log (η + ·309) = 143 + 1·0139 τ
VISCOSITY CENTIPOISES
DRY RUBBER CONTENT
3·20
3·10
3·00
2·90
2·80
2·70
2·60
2·50
2·40
2·30
2·20
2·10
2·00
1·90
1·80
1·70
1·60
1·50
1·40
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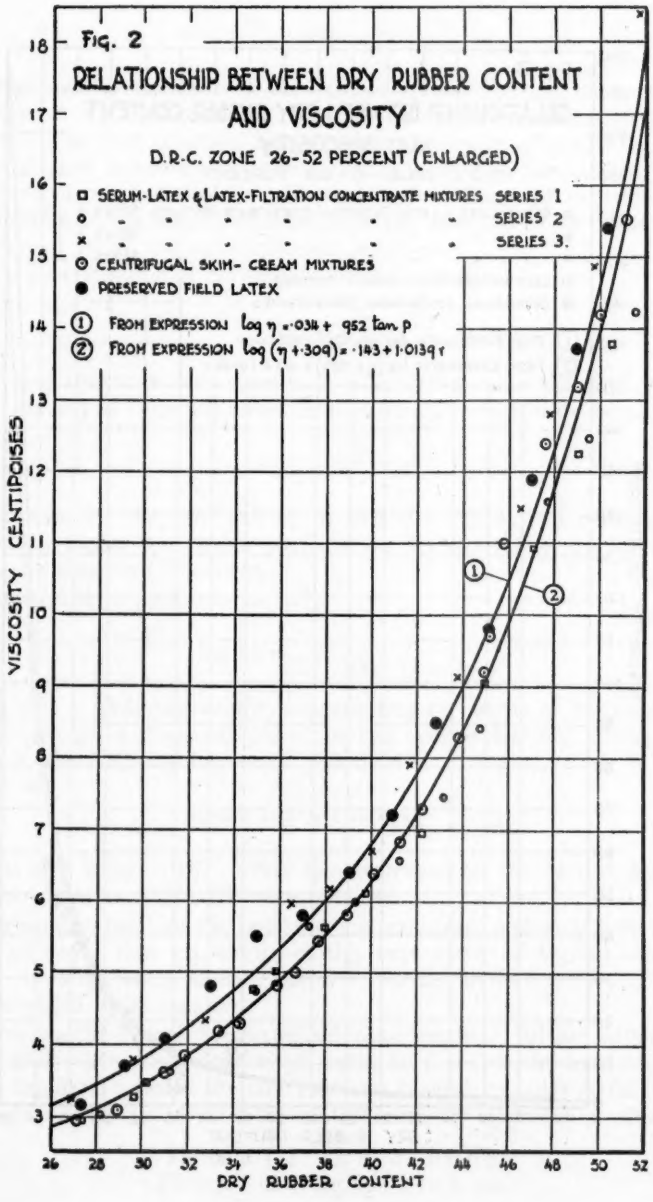
Fig. 2
RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY
D.R.C. ZONE 26-52 PERCENT (ENLARGED)
SERUM-LATEX & LATEX-FILTRATION CONCENTRATE MIXTURES SERIES 1
SERIES 2
SERIES 3.
CENTRIFUGAL SKIM- CREAM MIXTURES
PRESERVED FIELD LATEX
(1) FROM EXPRESSION log η = ·038 + ·952 tan p
(2) FROM EXPRESSION log (η + ·309) = ·143 + 1·0139 r
VISCOSITY CENTIPOISES
DRY RUBBER CONTENT
18
17
16
15
14
13
12
11
10
9
8
7
6
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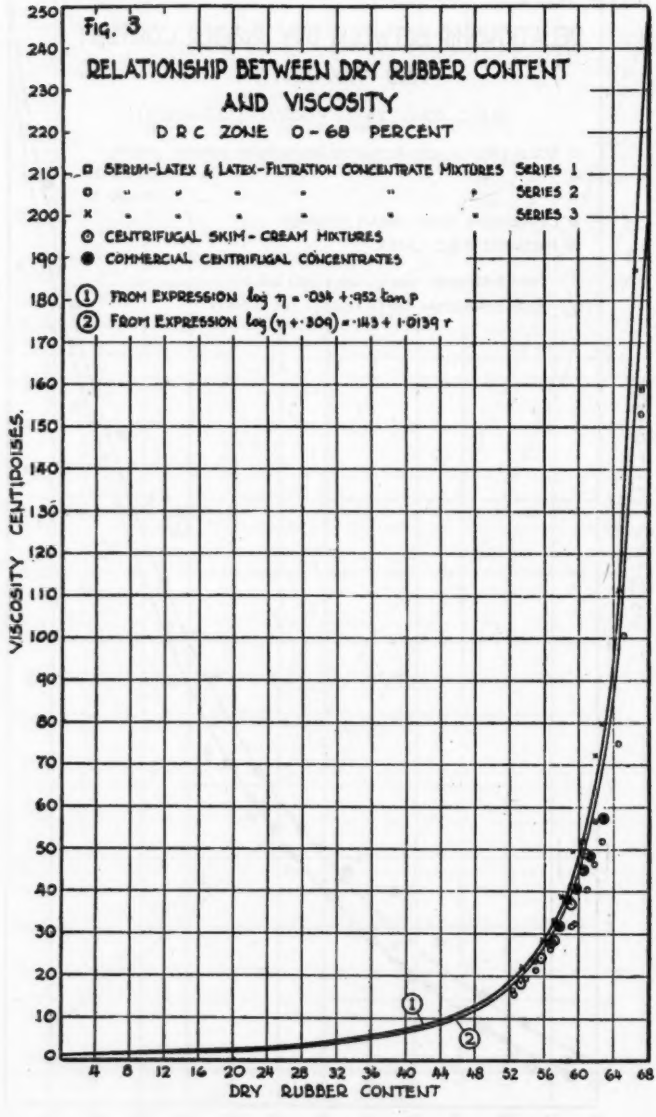


Fig. 3
RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY
D R C ZONE 0 - 68 PERCENT
□ SERUM-LATEX & LATEX-FILTRATION CONCENTRATE MIXTURES SERIES 1
○ " " " " " " SERIES 2
× " " " " " " SERIES 3
⊙ CENTRIFUGAL SKIM - CREAM MIXTURES
● COMMERCIAL CENTRIFUGAL CONCENTRATES
① FROM EXPRESSION log η = ·034 + ·952 log P
② FROM EXPRESSION log (η + ·309) = ·143 + 1·0139 r
VISCOSITY CENTIPOISES.
DRY RUBBER CONTENT
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 68

The formula of Hatschek:

$$n=\frac{n_0}{1-\Phi^{\frac{1}{3}}} \text{ and } n=\frac{n_0}{1-(h\Phi')^{\frac{1}{3}}}$$

where Φ represents the ratio of the volume of the dispersed phase to that of the solution, h is a hydration factor, and Φ' is weight concentration, were both considered. The first equation fails, because the graph of $n:(1-\Phi^{\frac{1}{3}})^{-1}$ should be a straight line, whereas the experimental data shows a pronounced curvature.

Constants of $n_0=1.06$ and $h=1.54$ were derived from the experimental data for application to the second equation, but the closeness of fit of the observed and calculated values was not considered satisfactory.

From a generalization of Hatschek's formula, namely:

$$n=\frac{n_0}{(1-\Phi^a)^b}$$

It was found that a is very close to 1. Calculation from the data in Series 3 gave a value of 1.01. For this series the best formula which could be derived was:

$$n=\frac{n_0}{(1-\Phi)^{3.666}}$$

The expression fits the data well up to 40% dry rubber and reasonably up to 50%, but for higher dry rubber contents the derived values are too low. This formula was, therefore, discarded.

A formula due to Arrhenius, namely:

$$\log n=n_0+K\frac{p}{100-(h+l)p}$$

in which h is a hydration factor compensating for water of hydration, and p is the percentage of dispersed phase, proved very interesting. Using the data in Series 3, the following expression was derived:

$$\log n=0.054+1.226\frac{p}{100-0.93p}$$

The value of h being -0.07. Using this expression on the data in Series 3, the results contained in Table III were obtained.

The agreement between the observed and calculated values is very good, and there is no doubt that expressions of this type could be applied satisfactorily to latex. It is obviously absurd, however, for the hydration factor, if such it should be called to be negative.

Without special regard to theoretical considerations, further attempts were made to find other expressions which could be fitted to the available data. A study of the data revealed the fact that two general formulas could be used to describe empirically the dry rubber content-viscosity relationship. These are:

$$\text{Formula (1)} \quad \log n=a+b\tan p.$$
$$\text{Formula (2)} \quad \log (n+a')=b+cr.$$

where r=ratio of dry rubber to serum$=\frac{\text{D.R.C.}}{100-\text{D.R.C.}}$, p=D.R.C. per cent, used as an angle in degrees and a, b and c=arbitrary constants of which a represents log n_0. For theoretical purposes, Formula (2) commends itself espe-

cially, for its application to latex means that relative changes in viscosity are proportional to the ratio of rubber to serum over the greater part of the range. The constant a' in this equation may be regarded as a correction factor for low values of n and r.

For purposes of estimation, however, Formula (2) is less convenient than Formula (1), which is by far the more convenient, although it is difficult to see any reason other than the purely empirical one for introducing the tangent of dry rubber content used as an angle.

TABLE III

D.R.C. (p)	Viscosity (Found)	Viscosity (Calculated)
0	1.00	1.13
3.2	1.19	1.24
6.7	1.37	1.39
9.4	1.52	1.51
15.3	1.96	1.87
20.2	2.36	2.29
26.9	3.26	3.12
29.6	3.80	3.59
38.2	6.19	6.04
41.7	7.91	7.75
49.7	14.09	15.38
53.7	22.05	23.44
58.0	39.18	39.63
62.1	72.30	71.94
62.6	79.84	77.98
64.8	111.4	113.5
66.4	186.8	152.8

Considering first the four series of concentrate-serum and concentrate-skim mixtures and pooling all the observations so as to arrive at an "average" expression for all four sets, the following expressions were derived:

$$\text{Expression (1)} \quad \log n = 0.010 + 0.942 \tan p.$$
$$\text{Expression (2)} \quad \log (n + 0.309) = 0.143 + 1.014\, r.$$

By using these two expression to represent the average regressions of D.R.C. on viscosity for the four series, the mean deviation and variance of deviations for each series was calculated, and is set out in Table IV.

TABLE IV

Series	Mean deviation from: Expression (1)	Mean deviation from: Expression (2)	Variance of deviations from: Expression (1)	Variance of deviations from: Expression (2)	No. of observations
1	− 0.003	− 0.005	0.528×10^{-3}	0.553×10^{-3}	27
2	− 0.014	− 0.017	0.314×10^{-3}	0.554×10^{-3}	25
3	+ 0.043	+ 0.040	0.647×10^{-3}	0.764×10^{-3}	29
4	− 0.005	− 0.006	0.602×10^{-3}	0.421×30^{-3}	31

It will be seen that the two expressions fit the data equally well. Expression (2) has been applied to each of the four series in turn, and because it is an "average" expression, it would be expected to fit Series 1 and Series 4 well, with some departure in opposite directions by Series 2 and 3. This is seen from the observed and calculated values to be the case. Series 3 from high-viscosity initial latex shows observed values higher than the calculated, while Series 2 shows higher calculated values.

To make a more exact fit, each series would require its own slightly different expression, but the average expressions represented by Expressions (1) and (2) fit the combined data for concentrate-serum mixtures reasonably well, and in the case of Expression (2) the proportionality between viscosity and the rubber-serum ratio is demonstrated. In this connection it is of interest to note that the satisfactory Arrhenius expression, to which reference was made earlier, is similar in type to Expression (2), except that the correction for curvature is introduced in a different place.

Having established the applicability of formulas of these types to the rather specialized series of mixtures prepared from four parent latices, it was next sought to obtain a similar expression based mainly on the determinations made on the 950 different samples of preserved field latex, for which figures are given in Table I, but also taking into account the 73 samples of centrifugal concentrate shown in Table II, as well as the values for the four series. To do this, the various groups need to be weighted to arrive at a reliable average regression. This is rather a difficult matter, because the loss of the detailed data for the samples of preserved field latex and centrifugal concentrates makes it impossible to determine statistically the effect of differences between places, conditions of tapping, or times of sampling. It is known, for instance, that the bulk of the samples of preserved field latex at D.R.C. 26-30% in Table I came from Kepong Estate, and it is not possible now to discover whether the rather low values obtained for these latices are due to the effect of mild slaughter-tapping, or whether they are merely characteristic of all latex from that particular source. From other knowledge available there is good reason to assume that the low values are due to the tapping system. In the absence of a better criterion for determining weights, a mean expression was arrived at by summing sums of squares and products within groups, so that each group is weighted according to the number of observations and the square of the range covered. This procedure leads to the expression which is called Expression (3), which is believed to be a reliable expression for the mean viscosity-D.R.C. relationship for all the data taken together. Expression 3 is as under:

$$\text{Expression (3)} \quad \log n = 0.034 + 0.952 \tan p.$$

It is felt that this equation should give a reliable indication of the viscosity of "average" latex of any dry rubber content. For the sake of convenience and easy reference, a viscosity table calculated from it has been drawn up, together with a similar table based on Expression (2). These tables form Table V. It will be noticed that the observed values for commercial centrifugal concentrates are in better agreement with the calculated values from Expression (2) than with those from Expression (3). This is not surprising, because the action of the centrifuge removes small agglomerates and tends to produce a latex viscosity rather lower than average. It is suggested therefore that the table based on Expression (2) is the more suitable for centrifugal concentrates.

It will be seen that, although the table based on Expression (2) is derived from mixtures from only four parent latices, the values do not differ very widely from those obtained from Expression (3), which is derived from results on a very large number of samples. Figures 1, 2, and 3 show the shape of the calculated viscosity curves, and their position in relation to the relevant experimental data. In Figure 3 the experimental points for viscosities below 15 centipoises have been omitted, because, owing to their number and the smallness of the scale, they would obscure the curves; they are, however, all shown in Figures 1 and 2, which permit the use of a more open scale.

TABLE V

VISCOSITY TABLES FOR LATEX AND LATEX CONCENTRATES AT 30° C.

D.R.C.	Viscosity (centipoises) calculated from: $\log n = 0.034 + 0.952 \tan p$.	Viscosity (centipoises) calculated from: $\log (n+0.309) = 0.143 + 1.014r$.
0	1.08	1.08
2	1.17	1.15
4	1.26	1.23
6	1.36	1.30
8	1.47	1.39
10	1.59	1.50
12	1.72	1.60
14	1.87	1.72
16	2.03	1.86
18	2.20	2.01
20	2.40	2.19
22	2.62	2.38
24	2.87	2.60
26	3.15	2.84
28	3.47	3.14
30	3.83	3.47
32	4.26	3.86
34	4.74	4.31
36	5.32	4.86
38	6.00	5.50
40	6.80	6.28
42	7.78	7.22
44	8.98	8.40
46	10.50	9.84
48	12.30	11.83
50	14.70	14.00
52	17.90	17.10
54	22.10	21.20
56	27.90	26.80
58	36.10	34.60
60	48.20	45.80
62	66.80	62.40
64	96.80	87.90
66	149.00	129.00
68	245.00	198.00

SUMMARY

Based on a large number of observations on preserved field latex and latex concentrates, mathematical expressions have been derived for the viscosity-dry rubber content relationship over the dry rubber content range 0-68%. It has been demonstrated that viscosity is proportional to the ratio of rubber to serum over almost the whole of the range. A viscosity table is presented, which it is hoped may serve as a datum line for the viscosity of "average" latex.

ACKNOWLEDGMENT

The author's grateful thanks are due to H. Fairfield Smith, statistician at the Rubber Research Institute of Malaya, for analysis of all the data and the derivation of all the mathematical expressions, and to K. C. Sekar and Che Abdul Wahid bin Abdul Wahab for much assistance in the experimental work itself.

PART II. VISCOSITY—TEMPERATURE RELATIONSHIP OF LATEX

INTRODUCTION

Published data on the viscosity-temperature relationship of latex is very sparse. Bächle (RUBBER CHEM. TECH. **10**, 675 (1937)) made viscosity measurements on 35% and 60% latices between the temperatures of 15° C. and 70° C., and concludes that in both cases the viscosity changes by from 2 to 3% for each degree of temperature change.

Further data on this relationship are now presented, together with the results of some preliminary experiments, which aimed at using viscosity as a means of detecting whether or not the state of the dispersion is changed fundamentally when latex is heated.

EXPERIMENTAL

All the measurements recorded in this paper were made with the Höppler Viscometer and the Höppler Ultrathermostat. For the temperature zone 15°-30° C., all determinations were made inside a large refrigerator; the viscometer and thermostat were placed bodily inside, and observations were made through specially fitted glass doors.

Observations were, in most cases, made at intervals of 5° C. between temperatures of 15° and 80° C.

All the latex used in the experiments contained approximately 0.5% ammonia.

The first trials were made with two different samples of centrifugal concentrate. In each case the original concentrate and a series of aqueous dilutions from it were all tested over the full temperature range above. Figures 5 and 6 show graphically the results obtained.

Further trials were also made with normal preserved latex and with a third sample of centrifugal concentrate. In each of these cases the latex was tested at intervals with temperature rising, and then also at intervals on cooling. In one case the latex was allowed to cool steadily, as soon as the viscosity had beeen recorded at the highest temperature (80° C.), and in the other the latex was held at 80° C. for several hours before being allowed to cool. Further reference is made to this work later in this paper.

DISCUSSION

VISCOSITY-TEMPERATURE

It will be observed from all the figures, and in particular from Figures 5 and 6, that when latex is heated from 15° C. this results in a sharp fall in viscosity. At higher temperatures, in the neighborhood of 60° C. the fall is less pronounced, and the viscosity-temperature curves tend to flatten out. Over the range 15°-80° C. the total fall in viscosity is in all cases of the order of 70% from the value at 15° C. With concentrated latex, Figures 5 and 6, the fall is much steeper between 15° C. and 20° C. than is the case with normal preserved latex (Figures 1, 2 and 3). The curves for similar samples are similar, but not identical in shape. It is usual for viscosity-temperature relationships to follow roughly a law of the general type:

$$Y = Ae^{bx}$$

This is the "compound interest" law. In the case of latex, however, this does not appear to apply, because on trial it is found that the relationship between viscosity and the logarithm of temperature is not linear.

The various types of latex do not respond identically to increasing temperature, the latices of high dry rubber content showing a much more rapid fall in viscosity in the initial stages of heating. This rapid fall is not however maintained, over the whole range of 15°-80° C. the mean percentage fall in viscosity per degree is within very small limits the same for all the types of latex examined, namely, of the order of 1.1% per degree Centrigrade. This figure is approximately half that found by Bächle. The low D.R.C. group of dilutions from centrifugal concentrate respond to heat in a manner very similar to the normal preserved latices, while the richer group show, in the early stages, values intermediate between the normal latex and the centrifugal concentrates.

It is not possible from the meagre data at present available to predict accurately the corrections which should be made for different temperatures, but it is suggested that for approximate use the following values might be taken:

TABLE I

	Fall in viscosity from value at 15° C. (per cent per degree) Zone					
Type of latex	15-20° C.	15-30° C.	15-40° C.	15-50° C.	15-60° C.	15-80° C.
Normal preserved	2.2	2.0	1.7	1.5	1.3	1.1
Centrifugal concentrate	3.8	2.7	2.1	1.8	1.5	1.1

On this basis a rough table for the comparative viscosities of commercial preserved latex and centrifugal concentrate can be drawn up for any desired temperature zone. The values for the temperatures 15° C., 20° C., and 30° C. which are the most likely to be required are:

TABLE II

COMPARATIVE VISCOSITIES AT DIFFERENT TEMPERATURES

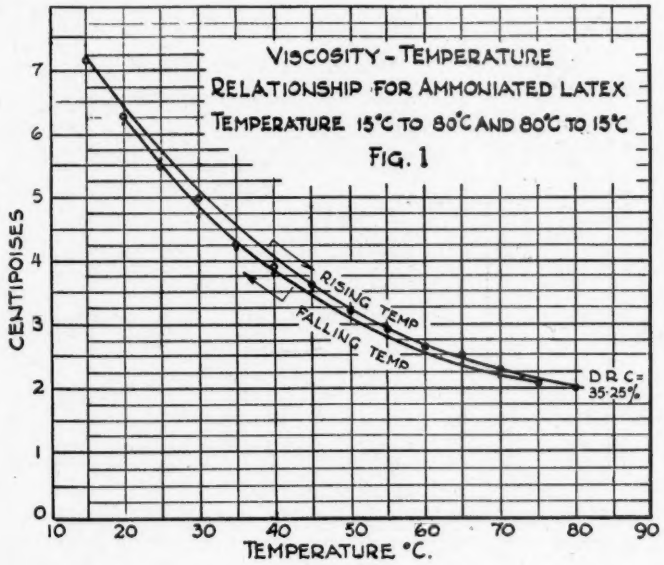
	Viscosity (centipoises)		
Type of latex	15° C.	20° C.	30° C.
Preserved Latex, Zone 30—40 per cent approx.....	5.0	4.5	3.5
	6.0	5.4	4.2
	7.0	6.3	5.0
	8.0	7.1	5.7
	9.0	8.1	6.4
	10.0	8.9	7.1
Centrifugal Concentrate, Zone 56—61 per cent approx.....	45.0	36.5	26.4
	50.0	40.5	29.8
	55.0	44.5	32.7
	60.0	48.6	35.7
	65.0	52.7	38.7
	70.0	56.7	41.7
	75.0	60.8	44.6
	80.0	64.8	47.6
	85.0	68.9	50.6
	90.0	72.9	53.6

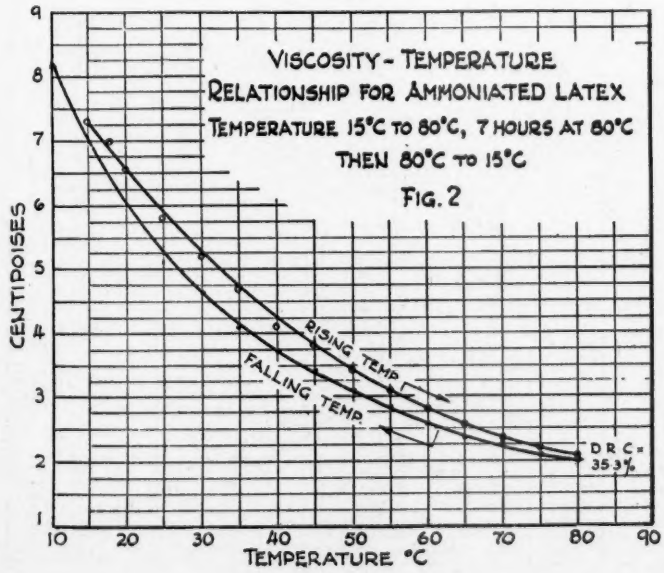
Similar tables for other zones can be constructed at will from the values in Table I.

VISCOSITY HYSTERESIS

It will have been observed from Figures 5 and 6 that the viscosity curves for the undiluted concentrates have a slight upward trend between the temperatures

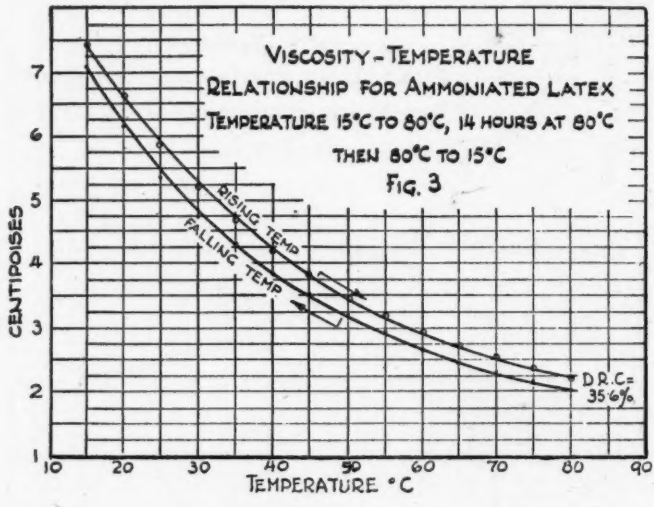
of 75 and 85° C. This would seem to indicate that on heating to these high temperatures a change in the state of the latex dispersion begins to take place.

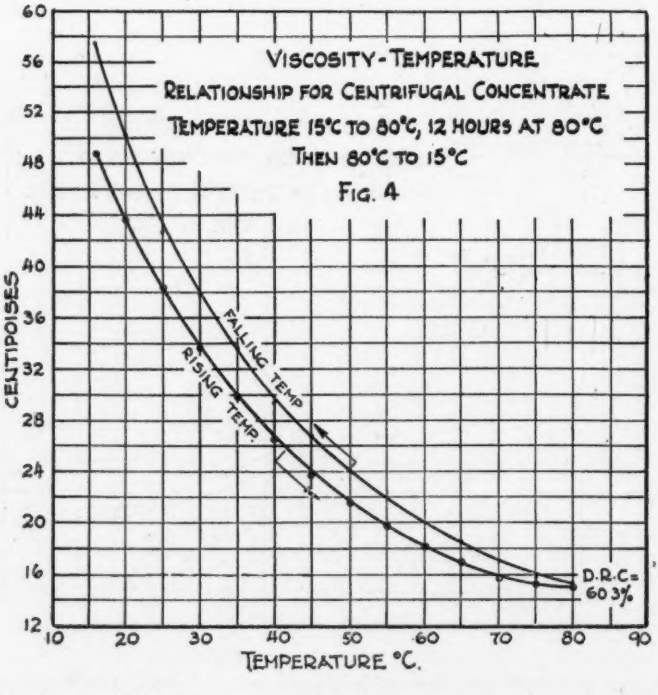




If the change is a real one, then on heating latex to a high temperature and later allowing it to cool, the viscosity curve for falling temperature should show appreciable departure from the curve for rising temperature.

A few trials were accordingly made with fresh ammoniated latex and freshly prepared centrifugal concentrate. The experimental results obtained are shown graphically in Figures 1 to 4 inclusive.

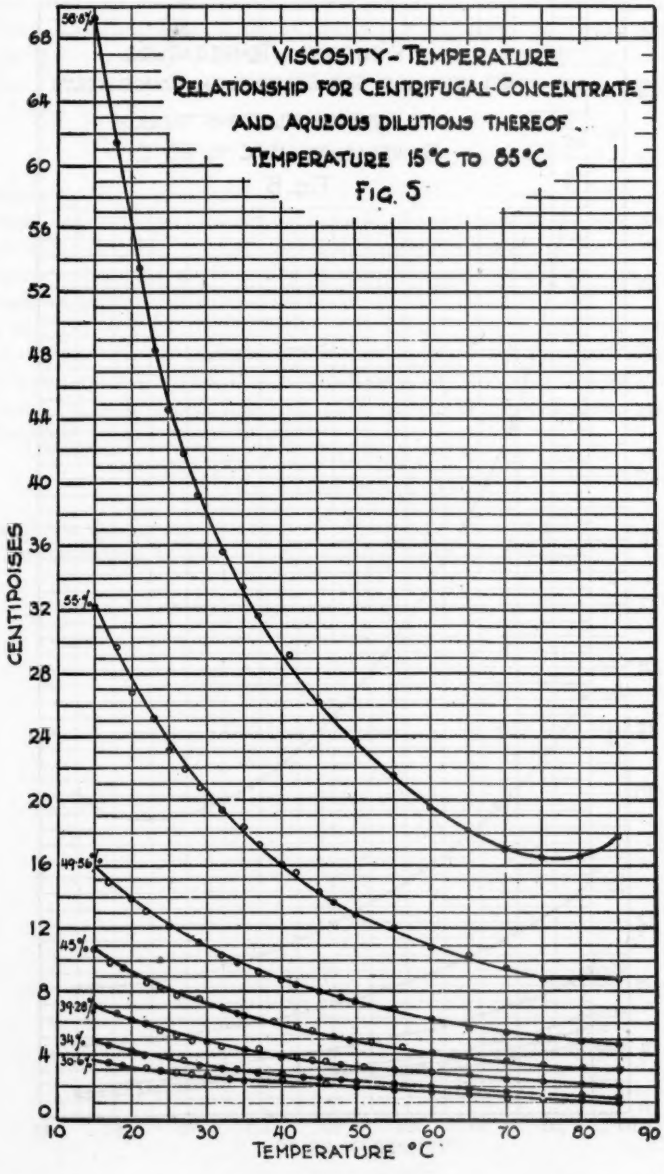




It will be observed from Figure 1 that when freshly prepared normal preserved latex is heated to 80° C and allowed to cool, the viscosity curves for rising and falling temperature lie very close to each other. The degree of hysteresis is

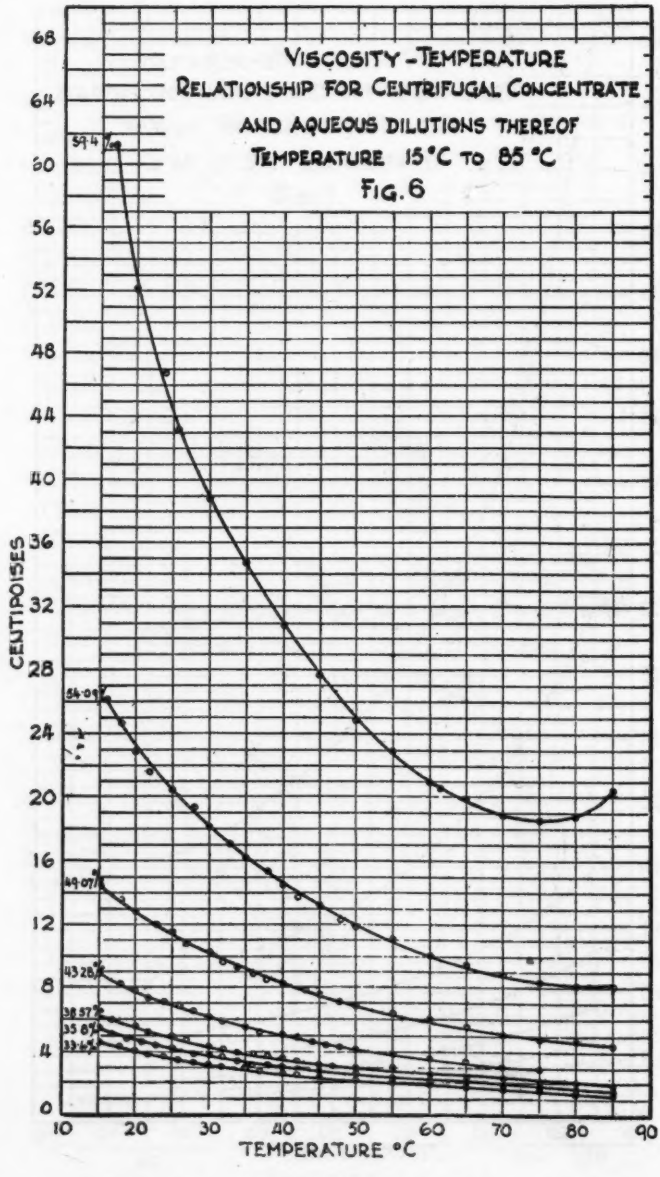
negligible. This would indicate that the state of the dispersion has not been changed materially.

When similar freshly preserved latex is heated to 80° C, and held at this



temperature for periods for 7 and 14 hours, respectively (see Figures 2 and 3) the cooling curves lie below and run almost parallel with the heating curve, indicating that the heating has brought about a slight but permanent reduction

in viscosity. The inference is that under the prolonged heating at 80° C some non-rubber substances, which contributed slightly to the viscosity, have been in part hydrolyzed by the ammonia to less viscous substances. Because the heat-



ing and cooling curves are so close together, and so similar with the cooling curve below the heating curve, it seems safe to assume that the heating has again not changed fundamentally the state of the dispersion.

When centrifugal concentrate is heated to 80° C, and held there for 12 hours before cooling, the results are somewhat different. The cooling curve now lies above the heating curve. At 80° C the viscosity, after 12 hours' heating, is not far removed from that recorded before the heating, but, as cooling proceeds, the heated latex becomes notably more viscous; at 15° C the difference in viscosity of the heated and unheated latex is nearly 9 centipoises. It would appear that with rich latex, prolonged heating at 80° C affects slightly the state of the dispersion. This result is in line with the inference drawn from the curves in Figures 5 and 6.

SUMMARY

The viscosity-temperature relationships for normal preserved latex, centrifugal concentrate and aqueous dilutions of such concentrates have been determined on a few samples. The results obtained suggest a basis for the calculation of approximate comparative viscosities for normal preserved latex and centrifugal concentrate at different temperatures.

From the viscosity curves for rising and falling temperatures on normal preserved latex and centrifugal concentrate, it appears that normal latex can be heated for several hours at 80° C without seriously affecting the state of dispersion. There are indications, however, that with rich concentrates, heating does affect the state of dispersion slightly.

ACKNOWLEDGMENTS

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PURIFIED LATEX AND RUBBER *

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INTRODUCTION

Within the past ten years purified rubber has come to be a subject of considerable interest, particularly in the field of electrical insulation[4, 6, 14, 85, 100, 116, 121]. Several papers have been published relating to methods of preparation and the properties of the resulting product. Numerous patents have been granted covering methods of preparation of purified rubber and its use in the manufacture of insulation[1, 3, 34, 36, 52, 63–73, 75, 123, 131, 134, 149], all such methods having as their object the removal of nitrogenous and water-soluble substances so that the final product may have a low degree of water absorption and high dielectric stability.

Previous investigators in this field have arrived at somewhat divergent conclusions as to the cause of water absorption, the proper requirements of a purified rubber in this respect, and the efficacy of the various methods of purification. Inasmuch as different lots of rubber or latex with different compositions and properties were used in each case, it is difficult to correlate their results. The object of this paper, therefore, is to review the earlier work and to offer new data and conclusions resulting from the application of several different purification methods to one original latex.

Until a few years ago all efforts to reduce the water absorption of rubber were through the use of pitches and resins together with fillers, waxes and the like[4, 7, 17, 20, 21, 23, 33, 38, 53, 57, 77, 78, 79, 84, 106, 118, 119, 148, 149, 157]. It was only about twenty years ago that the reason for deterioration of rubber insulation was traced to the absorption of water, and not until several years later that it was definitely attributed to the composition of the rubber itself. The first use of latex as such for insulation was described by Siemens[128] in 1863 and by Hancock[48] in 1864, who coated wires with either balata or *Hevea* latex.

Although the use of purified rubber in insulation has taken place within a comparatively few years, methods for purification date from about 1900. In 1898 Biffen[18] patented the centrifugal concentration of latex, and by such concentration removed a portion of the natural proteins and water-soluble components of the latex. Since that time centrifugal concentration and purification has been greatly improved and other methods such as creaming, filtration, dialysis, treatment with alkali and enzymes and heat hydrolysis have been subjects of considerable study.

The compositions of latex and sheet rubber have been given in detail by numerous observers. It is probable that latex particles carry an adsorbed film of protein[28, 64, 74, 147], together with many complex substances, including fat acids and their derivatives. In addition the liquid portion of the latex contains a large amount of other non-rubber substances, among which may be mentioned protein, fat acid substances, carbohydrates and water-soluble salts. De Vries[152] suggests that rubber is composed primarily of particles of hydrocarbon which carry a surface layer of adsorbed serum substances, consisting in part at least of proteins and lipoids, and that as the particles are aggregated by coagulation they carry

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with them a certain amount of serum substances, either in coagulated or entrapped condition and distributed through the rubber in a more or less continuous phase. It is this non-rubber substance which accounts for the high water-absorbing capacity of unpurified rubber, and hence of the insulation containing it.

I. METHODS OF PURIFICATION

Coagulation.—It is well known that the usual methods of plantation coagulation after dilution result in the removal of a large amount of water-soluble substances, together with a smaller portion of the proteins. If the rubber is prepared in the form of crepe, a further quantity of water-soluble solids will be removed because of the increased amount of washing[29, 54]. Belgrave[11] has noted a nitrogen content as low as 0.06% in a rubber from diluted latex coagulated with alcohol and washed.

The purification of rubber by flocculation of latex, as with metallic salts, has been the subject-matter of patents by Stutchbury[143], Stevens and Dyer[140], N. V. Rubber Culture Mij.[98] and others[22, 50, 59, 97]. The latex is slowly diluted to a low rubber content and their coagulated by means of metallic salts, such as calcium or zinc chlorides.

Washing.—Purification of rubber by merely washing it was the first method used[107], but this treatment is not sufficient to reduce its water absorption to a point where it is entirely suitable for insulation which must have high dielectric stability. Refinements in washing methods have been developed by Williams and Kemp[64, 156, 158], who find that soaking rubber in water for several days greatly increases the extent of purification. On the other hand, Boggs and Blake[16] find that washing with hot water for 4 hours after first soaking in water does not serve to deproteinise the rubber, and that its capacity for water absorption is not reduced. Recent work at the Rubber Research Institute of Malaya[122] has indicated that merely soaking fresh coagulum for two hours or more serves greatly to reduce its water-absorbing capacity. Other methods of washing freshly formed coagulum have been suggested[5, 57, 114].

Fractionation.—There are references[49, 96] in the literature to the purification of rubber by treatment with solvents to separate insoluble materials, and several patents[89, 134-6] have been issued based on this general procedure. None is adapted to large-scale production because of the difficulty attendant on manipulation of the rubber itself, the necessity of recovering the solvent and the soft product obtained.

Enzymes.—Enzymes have been used experimentally for the removal of proteins in latex. Trypsin was first used by Spence[133] and subsequently by Smith[137], and by Freundlich and Hauser[44] for this purpose. Gibbons and McGavack[47] used pepsin, trypsin or papain after stabilization of the latex against bacterial coagulation. Others have used enzymes alone or in conjunction with other methods, such as creaming, as a means of preparing purified rubber[41, 117, 120, 134, 137, 153].

Filtration.—Filtration as a method of purification has not been generally employed because of the tendency for the concentrate to clog the surface of the filter. Constant circulation of the latex does not entirely overcome the difficulty.

Alkali Hydrolysis.—One of the most effective means of removing the proteins in rubber is by treatment with alkalies[19, 25, 41, 43, 45, 53, 54, 58, 63, 70, 72, 97, 101, 115, 144, 158], thus causing their hydrolysis so that the degradation products may be easily removed by washing. Pummerer[102, 108, 112] and his coworkers have used this method extensively in preparing rubber containing extremely small amounts of

residual nitrogen. According to their procedure, latex is treated with sodium hydroxide at 50° C., after which the soluble products are removed by dialysis. Hydrolysis may be effected with other alkaline materials[65] or with salt solutions[31, 83, 93]. Care must be taken, however, to hydrolyze at as low a temperature as possible in order that the rubber may not be adversely affected. At high temperatures the purified product tends to become soft and sticky, so that it is no longer commercially useful.

After treatment at either low or elevated temperatures, it is necessary to remove the last traces of alkali. This may be done by dilution, coagulation and washing, or by preliminary dialysis of the latex to remove all soluble materials and subsequently coagulating and washing. It is difficult, however, to remove the alkali entirely by dialysis.

Hydrolysis by Heat. A number of methods have been developed for the hydrolysis of protein by subjecting latex or rubber to heat alone without the assistance of alkali or other chemicals. Park, Carson, and Sebrell[103] and Kemp[31, 32, 62, 63, 65] have subjected latex or rubber to treatment with water for several hours at a temperature of 150° C. After cooling and coagulating the latex with acetic acid, washing and drying, a nitrogen content of less than 0.1% is obtained. McPherson *et al.*[92] have made a detailed study of the extent of purification resulting from the treatment of rubber with water at 190° C., followed by washing in water and alcohol and drying in an inert gas at 110° C.

Centrifuging.—Centrifugal treatment of latex has been practised commercially as a means of effecting partial deproteinization[2, 59, 61, 80, 146, 151, 155]. Simple centrifuging of latex serves to remove a large part of the water-soluble substances as well as a portion of the insoluble materials. If the concentrate is diluted with water containing a small amount of ammonia and again centrifuged, a further purification is effected. Some of the protein material is also washed from the surface of the latex particles, and, together with more of the water-soluble substances, is removed in the dilute phase. This operation may be repeated several times, although the purification effected after about three treatments in the centrifuge becomes very small. Furthermore, the latex becomes increasingly sensitive to coagulation during the treatment. The method is satisfactory so far as the nature of the product is concerned, but may be relatively costly, due to the number of times the latex must be handled and the loss of rubber in the dilute phase.

Creaming.—Purification may be brought about by creaming latex, the result being similar to that of centrifuging. Natural creaming and consequent purification of latex was first described by Faraday[35]. Heim and Henriet[50] have described the creaming and purification of *Funtumia* and *Landolphia* latices by treatment with alum followed by washing, coagulation and repeated washing. Numerous patents have been granted for the the concentration and purification of latex, by special creaming methods[9, 40, 46, 87–91, 150, 155] or agents[86, 87, 152]. Studies of the creaming operation have been made recently by Baker[8] and by Stevens and Parry[142].

By observing certain precautions, normal latex may be creamed to a concentration of about 60%, after which it may be diluted with water and the creaming operation repeated as desired. An objection to creaming as a method of purification lies in the fact that, although the natural water-solubles and proteins are largely removed, a new water-soluble material, the creaming agent, is introduced, though in small amount.

Cataphoresis.—Stamberger and Schmidt[138] have described a method of purifying latex by subjecting it to electrodeposition, after which the deposit is re-

dispersed in ammonia solution and again electro-deposited. Pummerer and Kroepelin and others[55, 60, 76, 104-5, 125-7] have described methods of effecting electro-dialysis of latex.

Dialysis.—Beadle and Stevens[10] have claimed that 20 to 25% of the total nitrogenous material is dialyzable, together with a large amount of other water-soluble substances. More recently Stevens[139-141] and his associates have developed apparatus and a method for dialyzing latex, and they may at the same time effect concentration. They find that 80 to 85% of the diffusible impurities may be removed in a period of 8 to 9 hours at a temperature of 55° C., using two changes of soft water, and that substantially all the remaining impurities may be removed by further treatment. Dialysis has been used in conjunction with other methods[56, 59, 102].

Miscellaneous Methods.—Other than the methods above described, numerous methods have been proposed which effect partial purification of the latex or rubber. These comprise such means as treatment of the latex with adsorbing agents, such as charcoal[12], treatment with formaldehyde[26, 99, 130], treatment with alkali zeolite[30], heating with glycerol, etc.[45, 61, 94, 95, 124, 136].

Experimental.—The normal latex used in the preparation of all purified rubbers referred to below was of Malayan origin and had the following properties:

	Calculated on	
	Latex	Solids
Total solids	39.51%	100.0%
Dry rubber content	36.73	92.96
Ammonia content	.65	—
Acetone extract	1.60	4.05
Ash	.28	.71
Water-soluble substances	2.76	7.01
Nitrogen	.17	.42

In preparing rubber from the normal latex for water absorption, vulcanization and other tests, it was poured on levelled glass plates in quantity sufficient to produce sheets approximately 0.07 inch in thickness, and dried at room temperature in air.

The creamed latex was prepared by adding a solution of locust bean gum to the normal latex in an amount equivalent to 0.3% of dry gum on the latex solids, diluting the latex to a solids content of 30%, and allowing to stand for two days at room temperature. At the end of this time the serum was removed, the concentrate rediluted to 30% with a solution of gum equivalent to 0.2% on the concentrate solids, and the creaming was repeated. In the first and second concentrates a solids content of approximately 58% was obtained. Subsequent concentrations were increasingly difficult, and lower solids were obtained. In the fifth and sixth creaming it was necessary to warm the latex to 40° C. to obtain a satisfactory concentration. For preparation of the rubber samples the concentrates were dried on glass as for the normal latex.

The centrifuged concentrates were made in a commercial DeLaval machine, especially adapted to latex concentration. The normal latex was first diluted to 30% concentration with water and the ammonia content was brought to 0.5%. The machine was adjusted to produce a concentrate of slightly over 60% solids and a skim of about 10% for the first concentration. In subsequent concentrations the amount of solids passing into the skim dropped to below 1%. By repeating the dilution of the latex and adjusting the ammonia content, repeated concentra-

tion and purification of the latex was made. Beyond the third concentration, however, some difficulty was encountered, due to the tendency of the rubber to coagulated within the centrifuge, even though the amount of ammonia was increased slightly. In the eighth concentration it was found impossible to bring the solids content in the concentrate above 50% without coagulation. Films of the rubber were prepared by drying in air as above described. Several days were required, however, for drying the concentrates which had been treated four or more times.

In purification by dialysis an apparatus similar to that described by Stevens but consisting of only one latex cell between two water cells each 15 inches square and $\frac{3}{4}$ inches in thickness, was used. The latex cell was filled three-quarters full with the normal latex and dialyzed with running water at 20° C. for 40 hours. The latex was diluted somewhat during this period, since no attempt was made to maintain it at constant volume. After dialysis, sheets of rubber were obtained by drying as above described.

In hydrolyzing the latex proteins by means of alkali, sodium hydroxide solution was added in an amount equivalent to 2% on the latex, which was then heated to 55° C. for five hours. The latex was allowed to cool, and the serum layer, which was brown, was removed. The concentrate was then diluted to 10% solids and coagulated with 1% acetic acid; the coagulum, which separated rapidly, was soaked for two periods of four hours each with change of water, after which it was sheeted and dried in air. No special precautions were taken to prevent oxidation other than drying at low temperature and preventing direct exposure to sunlight.

Three different lots of purified rubber were prepared by direct coagulation from the normal latex. The first lot was prepared by diluting the normal latex with water to 4% solids content, and then coagulating with 1% acetic acid solution, which was added until a *p*H of 4.6 was reached. After standing for several hours, the coagulum collected at the top of the serum and was separated. After sheeting, it was soaked in water for two periods of one day each with a change of water, and then dried at room temperature. A second sample was prepared in a similar manner, except that the latex was diluted to 1% solids before coagulation. In the third lot, the latex was diluted to 4% solids and then flocculated with 0.5% solution of zinc chloride previously acidified to a *p*H of 6.0.

Discussion of Results—The composition of the several purified rubbers is shown in Table I. The most complete elimination of nitrogen and water solubles resulted from alkali hydrolysis. However, as will be shown below, this rubber does not give results in the water-absorption test which compare favorably with those obtained from some of the other purified rubbers. Furthermore, it becomes tacky during drying, even at room temperature.

As is to be expected, dialysis removed the larger part of the water solubles (approximately 93%) but only about 20% of the total nitrogen. This method would appear to be most useful in conjunction with prior hydrolysis of the protein rather than as a separate process.

Centrifugal treatment of the latex is much more efficient than an equal number of creaming operations, although the cost of centrifuging is undoubtedly greater. Bearing in mind that in commercial operation it is not practicable to cream or centrifuge more than three or four times, it is of interest that the rubber made by coagulating diluted latex, followed by soaking in fresh water, compares favorably as to water solubles with latex centrifuged six times, although the

nitrogen and ash contents are higher. Comparison of these rubbers as to water absorption is also of interest. (cf. Table II.)

The difference in results obtained by diluting the latex to 1% and 4% solids is not great, probably due to the strongly adsorbed residual layer of non-rubber substances on the latex particles and possibly to the coagulation of some of the serum proteins.

The rubber prepared by a flocculation with zinc chloride has a water-soluble content higher than would be expected. The unusually high ash content is due to both the formation of zinc hydroxide and the combination of zinc chloride with proteins.

TABLE I

Rubber	Nitrogen [a] %	Water Solubles [b] %	Ash %	Acetone Ext. %
Normal latex	0.42	7.01	0.71	4.05
1 × creamed latex	0.28	—	0.25	3.21
2 × " "	0.20	2.06	0.12	2.58
3 × " "	0.13	1.25	0.079	1.85
6 × " "	0.10	0.5	0.09	1.72
1 × centrifuged latex	0.16	2.14	0.140	1.90
2 × " "	0.09	1.11	0.071	1.89
3 × " "	0.08	0.76	0.040	1.85
4 × " "	0.08	0.66	0.025	1.74
5 × " "	0.07	0.67	0.015	1.67
6 × " "	0.07	0.45	0.009	1.50
8 × " "	0.06	0.30	0.005	1.53
Dialyzed latex	0.30	0.72	0.307	3.37
Alkali-treated	0.02	0.16	0.115	2.03
Latex diluted (4%)	0.17	0.36	0.09	2.53
" " (1%)	0.15	0.26	0.05	2.65
Flocculated latex	0.06	0.65	2.65	2.21
Crepe (RCMA-Wmk.)	0.32	—	0.15	—
Sheet, Type 1, Estates	0.41	—	0.26	—

[a] Gunning-Kjeldahl method.
[b] Method of Fowler[42].

II. WATER ABSORPTION

It has been stated that the water-absorbing capacity of a purified rubber is the most important single criterion in determining its suitability for insulation. The difference between ordinary rubbers and deproteinized rubber in this respect becomes evident when thin sheets are exposed to water either at room temperature or elevated temperatures. Several tests have been proposed as a method of measuring the water-absorption of rubber[24, 27, 93, 101]. Boggs and Blake[15, 16] use a test sheet of approximately 2 mm. thickness, this being soaked in distilled water for 20 hours at 70° C. Under the conditions of the test they find that commercial rubbers absorb up to 30 mg. per square inch, whereas purified rubbers absorb only up to about 5 mg. per square inch. The amount absorbed increases with increasing temperature. Boggs and Blake's test for water absorption has been criticized by Kemp as not adapted to show the difference in water-absorption of various types of rubber, and he prefers the use of a much longer period of immersion. Lowry and Kohman[82] and Skinner and Drakeley[132] have made exhaustive studies of the absorption of water by rubber.

As to the exact cause of water absorption in rubber, there is no generally accepted opinion. As has been stated above, Kemp[62] is of the opinion that the extent of water absorption is dependent primarily on the osmotic pressure of

the external liquid and the molecular concentration of the water solubles within the rubber, water slowly passing into the internal solution and tending to do so to infinite dilution. Messenger and Scott[93] find, on the contrary, that water absorption is due to both proteins and water solubles; they recognize, however, the prominent part played by the osmotic effect of the water solubles alone. Boggs and Blake maintain that water absorption is due primarily to proteins naturally present in the rubber, which are known to be hydrophilic.

Experimental.—Films of the several types of purified rubbers were prepared, as described above, by drying the treated latex on glass to produce films approximately 0.07 inch thick. In the case of coagulated rubbers, sheets were hot-pressed between aluminum to the same gauge. The sheets were then soaked in distilled water for 20 hours at 70° C. (Boggs and Blake method) and for three weeks at room temperature. The amount of water absorption in milligrams per square inch of surface was determined at the end of the twenty-hour period and at the end of seven, fourteen and twenty-one days at room temperature. The results are shown in Table II and graphically in Figure 1.

Discussion of Results.—The data obtained indicate that the removal of both protein and water-soluble matter is important in preparing rubbers of very low water-absorbing capacity. There is no direct relationship between the water absorbed and the amount of either nitrogen or water-soluble material, although it is true that with a high content of either the water-absorption is high. There is an apparent discrepancy in the case of the alkali-treated rubber, but probably this is due to surface oxidation, as mentioned above; it is known that water absorption increases as oxidation progresses.

In order thoroughly to evaluate purified rubbers as to water absorption, it is desirable to extend tests over a much longer period, as Kemp has indicated. For comparative purposes, however, the tests as made clearly differentiate between the several samples.

The results show that centrifuged and creamed concentrates are about equal, but that continued centrifuging is more effective than continued creaming, as judged by tests in either hot or cold water. The sample prepared by flocculation, and having a low nitrogen content, has a water absorption value between that of once- and twice-centrifuged latex. The samples prepared by coagulation of diluted latex have a value equal to or slightly better than that of twice-centrifuged latex. These water absorption values will be further compared with values obtained after vulcanization.

III. VULCANIZATION AND AGING OF PURIFIED RUBBER

The effect of the removal of the nitrogenous and water-absorbing materials on the vulcanization characteristics of the rubber has been investigated by several workers, but there is no general agreement as to the influence of these materials, particularly of the protein. Beadle and Stevens[10] and others[25,101] find that rubbers relatively poor in nitrogen vulcanize slowly, yielding a poorer vulcanizate than in the case of rubber containing a normal amount of nitrogen. Pummerer and Pahl[112], Feuchter[37] and Boggs and Blake[16] find that purified rubber has normal vulcanization characteristics.

Experimental.—In the present investigation four types of purified rubber have been compared, in behavior on vulcanization, with a whole latex rubber made from the same original latex and with standard grades of smoked sheet and pale crepe. Samples of the purified rubbers obtained by evaporation or coagulation were compounded on the mill in the usual manner and vulcanized in a press

TABLE II

WATER ABSORPTION

Source of rubber	20 hrs. at 70° C. (Mg./sq. in.)	Room temp. 7 days (Mg./sq. in.)	Room temp. 14 days (Mg./sq. in.)	Room temp. 21 days (Mg./sq. in.)
Normal latex	102	22	32	38
3 × creamed latex	11	6	7	9
6 × " "	7	4	6	6
1 × centrifuged latex	30	18	23	25
2 × " "	20	8	10	12
3 × " "	11	5	6	7
6 × " "	4	2	3	4
8 × " "	3	3	3	3
Dialyzed latex	41	15	—	—
Alkali-treated latex	35	15	16	—
Latex diluted (4%), coagulated	20	9	10	10
Latex diluted (1%), coagulated	18	7	10	11
Flocculated latex	26	21	—	—
Crepe (RCMA-Wmk.)	18	—	—	—
Sheet	26	—	—	—

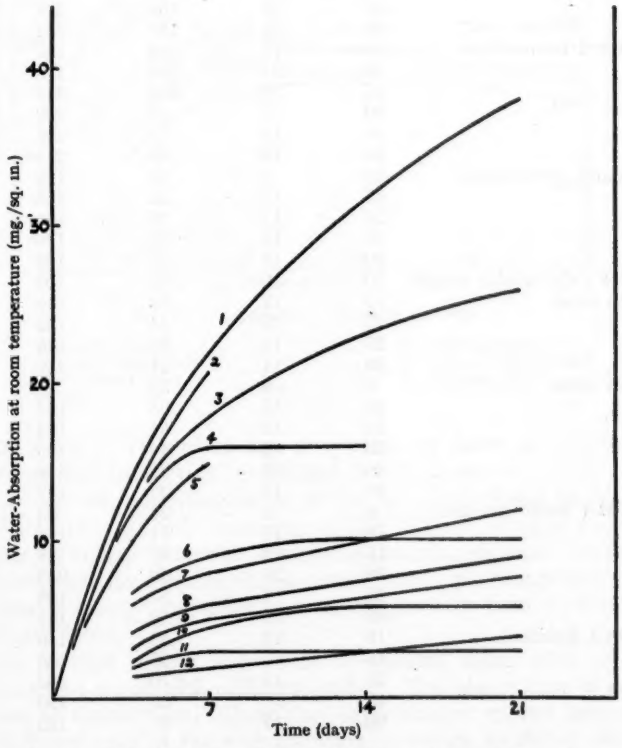

FIG. 1.—Water-Absorption of Purified Rubbers at Room Temperature.

1. Normal latex
2. Flocculated latex
3. 1×centrifuged latex
4. Alkali-treated latex
5. Dialyzed latex
6. Diluted latex (4% solids)
7. 2×centrifuged latex
8. 3×creamed latex
9. 3×centrifuged latex
10. 6×creamed latex
11. 6×centrifuged latex
12. 8×centrifuged latex

for periods up to 60 minutes at 40 lb. steam pressure (142° C). The vulcanizing data are shown in Table III and Figure 2.

A further comparison has been made showing the difference in vulcanization

TABLE III

VULCANIZATION OF PURIFIED RUBBER

Rubber	100
Zinc oxide	3
Sulfur	2
Stearic acid	0.5
Mercaptobenzothiazole	0.75
Flectol H	1

Rubber	Vulcanized Min. at 142° C.	Modulus (kg. per sq. cm.) 500%	Modulus (kg. per sq. cm.) 700%	Tensile strength (kg. per sq. cm.)	Elongation %
Normal latex	5	29	135	203	730
	10	42	194	235	740
	15	46	206	294	770
	30	48	171	260	750
	45	37	154	228	770
	60	32	157	234	800
1 × centrifuged concentrate	5	15	55	183	890
	10	21	109	215	825
	15	22	102	243	830
	30	22	87	228	840
	45	19	74	205	850
	60	19	69	211	860
6 × centrifuged concentrate	10	9	26	115	980
	15	11	25	163	970
	30	11	25	166	860
	45	10	23	170	1010
	60	11	17	163	1010
Diluted latex (4% solids) coagulated with acid.	10	10	24	102	970
	15	12	33	140	930
	30	15	44	162	920
	45	15	34	146	920
	60	14	31	140	940
6 × creamed latex	5	9	23	115	995
	10	16	63	152	880
	15	15	51	194	910
	30	16	44	155	910
	45	15	38	158	900
	60	15	32	147	915
Crepe (RCMA water-marked)	5	9	24	83	940
	10	19	71	154	835
	15	19	68	188	850
	30	20	69	203	870
	45	19	57	198	890
	60	19	56	181	890
Sheet (Type 1 Estates)	10	13	53	140	890
	15	17	58	156	860
	30	19	70	183	850
	45	19	63	190	880
	60	17	57	175	890

characteristics between rubbers obtained from once- and thrice-centrifuged latex at two different temperatures. In this instance a different mixing particularly adapted to low temperatures was employed. The results are shown in Table IV and Figure 3.

Data on the aging characteristics of the vulcanized, purified rubbers referred to above are given in Table V. The aging tests were made on standard test-pieces, aged in the oxygen bomb at 70° C. and 300 lb. per square inch (21 kg. per sq. cm.) pressure for the periods indicated.

The data in Table III clearly illustrate the difference in vulcanization characteristics between the purified and other rubbers. The difference in rate of vulcanization, tensile strength and other physical properties is approximately in proportion to the extent of purification effected. The rubber from once-centrifuged latex vulcanizes faster and has a higher tensile strength than either crepe or sheet, but with increasing purification the tensile strength becomes less than that of crepe or sheet; the rubber from latex creamed 6 times has about the same vulcanization characteristics as crepe. The behavior of rubber from diluted latex is abnormal if judged solely on the nitrogen and water-solubles content

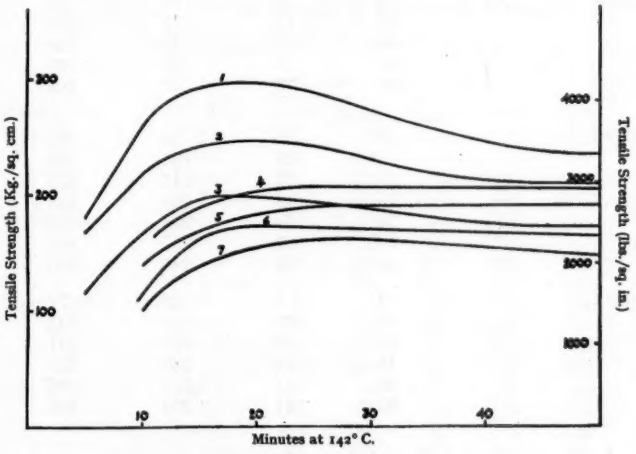

FIG. 2.—Vulcanization of Purified Rubbers.

1. Normal latex
2. 1×centrifuged latex
3. 6×creamed latex
4. Crepe
5. Smoked sheet
6. 6×centrifuged latex
7. Diluted latex

as shown in Table I. Its vulcanizing properties are those of a highly purified rubber, such as that from latex centrifuged 6 to 8 times.

Purified rubber will not vulcanize at 80° C. to a vulcanizate having optimum qualities (Table IV). It will vulcanize at 100° C. but requires approximately twice as long as rubber prepared from once-centrifuged latex. Incidentally, it has been found that latex compositions made from triple-centrifuged latex show much less tendency to prevulcanize at room temperature than do those from the once-centrifuged latex.

Vulcanized purified rubber withstands accelerated aging tests in a manner comparable to that noted with ordinary rubber. This observation is contrary to the statement of Okita[101] and others that deproteinized rubber generally shows increased oxidation even at room temperature, although, as stated above, alkali-purified rubber does so oxidize. The purified rubbers show poorer aging than does normal latex rubber, but the values for crepe, sheet and rubber from latex creamed or centrifuged six times, are nearly the same. As in the tensile tests,

TABLE IV

VULCANIZATION OF PURIFIED RUBBER

Rubber	100
Zinc oxide	1
Sulfur	2
Piperidinium pentamethylenedithiocarbamate	0.75

Rubber	Vulcanized Min. at 80° C.	Modulus (kg./cm²) 500%	Modulus (kg./cm²) 700%	Tensile strength (kg./cm²)	Elongation %
1 × centrifuged	0	26	78	167	800
	20	29	113	245	850
	40	34	137	355	910
	80	36	143	339	910
	100	40	177	355	870
3 × centrifuged	0	9	28	71	850
	40	17	71	252	940
	80	16	73	230	950
	140	17	92	248	880
	200	17	97	288	920
	Min. at 100° C.				
1 × centrifuged	0	26	78	167	800
	5	33	125	250	865
	10	37	146	375	880
	15	38	188	383	840
	20	48	206	365	840
	30	69	257	395	820
	45	69	280	390	780
3 × centrifuged	0	9	29	72	880
	15	24	130	303	860
	30	39	197	331	800
	45	44	230	375	800
	60	31	254	390	800
	90	44	230	360	790

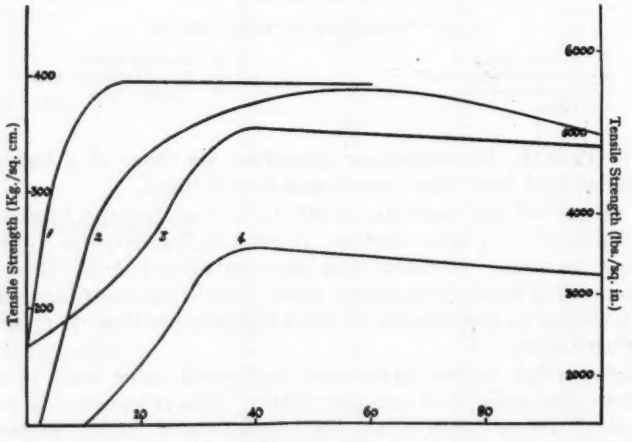

FIG. 3.—Vulcanization of Rubber from Centrifuged Latex.
1. 1×centrifuged latex, 100° C.
2. 3× " " 100° C.
3. 1× " " 80° C.
4. 3× " " 80° C.

the aging test on rubber from diluted latex shows an unexpected behavior, being similar to that of highly purified rubber.

The water absorption tests on the vulcanized, purified rubbers (Table VI) are of special interest.

The order of decreasing water-absorption values is slightly different from that of the unvulcanized samples, in that the rubber from diluted latex is the best of the series. It will be observed also that the order of water absorption values of the vulcanized samples is in the same order as their water-soluble contents, whereas in the unvulcanized samples it is nearly in the same order as their nitrogen contents. It appears therefore that, although proteins may be the

TABLE V

AGING TESTS ON VULCANIZED PURIFIED RUBBER

(Oxygen bomb 70° C., 300 lb. pressure)

		Unaged		Aged 96 hrs.		Aged 168 hrs.	
Source of rubber	Vulc.	10/40	15/40	10/40	15/40	10/40	15/40
Normal latex	500%	42	47	105	107	117	107 kg./cm.^{2}
	700%	194	196	—	—	—	—
	Break	235	232	320	322	285	260
	% Elong.	740	760	685	695	655	650
1 × centrifuged latex ...	500%	21	27	55	58	65	57
	700%	105	126	263	268	—	245
	Break	216	214	280	295	251	245
	% Elong.	835	790	715	735	695	700
6 × centrifuged latex ...	500%	9	9	20	28	24	26
	700%	26	26	100	148	126	168
	Break	116	130	245	255	200	216
	% Elong.	980	950	855	800	780	745
Diluted latex (4%).....	500%	10	13	21	30	22	28
	700%	24	38	73	129	88	132
	Break	98	137	145	218	135	158
	% Elong.	68	935	840	805	785	730
6 × creamed latex	500%	15	18	34	40	39	43
	700%	63	65	171	201	205	213
	Break	152	154	266	279	222	213
	% Elong.	880	850	785	785	715	700
Crepe (RCMA-WMK.).	500%	19	20	34	50	53	55
	700%	77	83	167	220	—	—
	Break	154	177	261	271	221	207
	% Elong.	835	830	800	750	690	670
Sheet (Type 1, Estates).	500%	13	196	29	42	29	43
	700%	53	74	126	184	130	175
	Break	140	161	224	265	165	177
	% Elong.	890	860	815	775	760	700

controlling factor in water absorption of unvulcanized rubber, they are so modified during vulcanization as to render them less effective, the water-soluble substances then becoming the predominant factor.

Summary and Conclusions.

Of the methods of purification employed, the most effective, determined by the amount of nitrogen, ash and water-soluble material remaining in the rubber is alkali-hydrolysis, although the product is readily oxidizable. Centrifugal treatment is more effective than creaming, and if repeated several times, yields a product similar to the alkali-treated rubber. Coagulation of diluted latex followed

by soaking the coagulum in water, is equivalent in elimination of non-rubber substances to one or two centrifugal treatments. Only partial purification results from flocculation or dialysis.

From the viewpoint of its practical application, the water absorption value of purified rubber after vulcanization is a more important consideration than its non-rubber content alone. While water-absorption is related to the amount of protein, ash and water-soluble substances present in rubber, a low content of

TABLE VI

WATER ABSORPTION OF VULCANIZED PURIFIED RUBBERS

Vulcanized 20 min. at 140° C.

Source of Rubber	Water-absorption at 70° C. (mg./sq. in.) 20 hrs.	48 hrs.	168 hrs.
Normal latex	52	75	131
1 × centrifuged latex	20	26	46
6 × centrifuged latex	6	9	15
6 × creamed latex	8	12	18
Diluted latex (4%) coagulated	5	6	9
Crepe	13	16	27
Smoked sheet	12	15	24

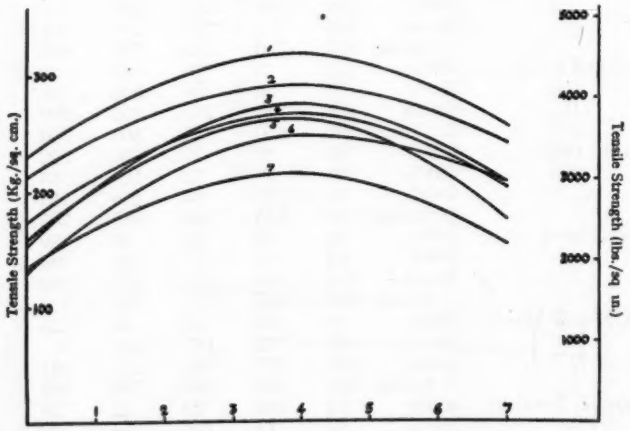

FIG. 4.—Aging Characteristics of Purified Rubber.

1. Normal latex
2. 1×centrifuged latex
3. 6×creamed latex
4. Crepe
5. Smoked sheet
6. 6×centrifuged latex
7. Diluted latex

any one of these is no assurance that the water-absorbing capacity of the vulcanized rubber will be low. In unvulcanized rubber the water-absorption is proportional to the protein content, whereas in vulcanized samples it is proportional to the amount of water-soluble substances.

The rate of vulcanization, tensile strength, modulus and aging properties of purified rubbers show a general decrease with decreasing content of non-rubber substances, a tendency particularly to be observed in the case of centrifuged and creamed latex rubber. However, the physical test values of the vulcanized

rubbers are more closely parallel to the water absorption values than to the non-rubber content.

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FICUS ELASTICA AND CASTILLOA LATICES *

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Although for all intents and purposes the *Hevea Brasiliensis* or Para rubber tree is the only rubber-yielding tree at present cultivated, this was not always the case. Today the words rubber and latex are almost synonymous with Para rubber and Para latex, but there was a time when rubber from other sources was available and the quality of commercial raw rubber showed very large variations.

HEVEA LATEX AN EXCEPTIONAL TYPE

Owing to the present predominance of rubber from *Hevea Brasiliensis*, almost all chemical investigations have been concentrated on the latex from this tree and the rubber therefrom, and a position has been reached which tends to the assumption that *Hevea* latex and rubber are the normal types, while others are abnormal. Thus, as is well known, *Hevea* latex is readily coagulated by a very small addition of an electrolyte and coagulates spontaneously in the country of origin in about 12 or 14 hours unless an antiseptic or preservative be added. It is therefore assumed that a latex which is not readily coagulated by electrolytes or does not coagulate spontaneously is abnormal whereas as a fact, the reverse is the case. If an examination is made of latices of other botanical origin, rich in hydrocarbon, it will be found that the best known of these are not coagulated either spontaneously or with the aid of electrolytes. Consequently it may be concluded that *Hevea* latex is exceptional and abnormal. Unfortunately much of the data in regard to other latices is scanty and unreliable. Only in a few instances have we the records of trained chemists[2]. Most of the information is based on statements of observers without scientific training or at least without adequate chemical experience. Therefore any contribution to our knowledge of latices other than that of *Hevea* is very welcome.

COMPARISON AS A SOURCE OF RUBBER

In a recent issue of this journal was published a paper by Daniel, Freundlich and Söllner on the "Stability of *Ficus Elastica* Latex"[3]. However, as some of the statements made and the conclusions reached are not in agreement with my own experience of this latex, it is worth while putting on record certain observations which I made many years ago, with fresh latex on the spot, which have not previously been published. These also provide some additional data bearing on this latex.

In the early plantation days, *e.g.*, up to 1905 or 1910 when the present developments in the Far East were in their infancy, there was no certainty as to the best species of rubber tree to plant. The bias was in favor of *Hevea* as it yielded the Para rubber, the acknowledged best quality of rubber on the market. It is probable, however, that not this, but the discovery of wound response was the reason for the survival of *Hevea* as the source of plantation rubber. The *Hevea* yields little or no rubber at first tapping and that of a very viscous nature.

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After a few days a gradually increasing amount is obtained until at the end of ten days or a fortnight the tree is yielding normally. So far as I am aware no other tree behaves in this manner. The bulk of the latex from other botanical sources is obtained in a few tappings, and the trees are then rested for months before more latex can be obtained. At least this is the view generally held, and I am not aware of any systematic tests on repeated tappings at short intervals. Rubber yielding trees other than *Hevea* suffer from other economical disadvantages; thus the *Manihot* or *Ceara* was found to have a very hard bark or outer layer of cortex which had to be removed before tapping could be begun. With *Ficus* the latex vessels are deeply embedded, many in the wood; consequently deep cuts are required to give an adequate flow. This results in damage in the cambium.

Most of the rubber trees other than *Hevea* which were planted in the early days have now been cut out to make room for the commercially profitable type, but when I visited the Malay peninsula in 1908 I had the opportunity of carrying out some of the first experiments ever made with rubber latex[4], both from *Hevea* and other latex-yielding species. These included a row of Rambong (*Ficus elastica*) trees which were available for tapping.

TAPPING *FICUS* TREES AND LATEX FLOW

Daniel, Freundlich and Söllner refer to the behavior of a tree tapped for the latex supplied to them, as reported by the manager of an estate. It was stated that the latex oozed freely at first, but quickly thickened and became apparently half coagulated. In my experiments this apparent tendency to coagulate was also noted in one instance. Actually it is not a coagulation in the sense in which this term is used for rubber latex, that is, a setting of the whole latex to a gel-like mass of spongy consistency, but a creaming and partial clotting. I find from my notes that as a general rule the latex exuded freely and more quickly than when *Hevea* trees are tapped. The latex appeared to be "thinner," that is, more mobile. On one occasion, however, I observed that the latex was thick and inclined to clot. I have noticed a similar behavior with *Hevea* latex and will refer to this later.

I had the services of a skilled Javanese tapper who had had experience in tapping *Ficus* trees. The cuts he made were deep and somewhat at random or rather in such positions as enabled him to collect the latex more easily, although inevitably a quantity was lost. This arises from the habit of the trees, which, like the famous Banyan tree, throws out aerial rootlets that take root in the ground and grow to subsidiary trunks. If a herringbone system was adopted as reported by Daniel, was it applied to several trunks or only to the central trunk? A photograph of one of the trees which were tapped for me will be found on page 32 of my little book on rubber[5]. Nothing was added to the latex which I collected in the way of a preservative, as nothing is necessary. *Ficus* latex keeps indefinitely, *i.e.*, does not putrefy, although it creams. The cream may become compacted, and eventually a solid irreversible clot or lump of irregular outline may form in the latex; much of it, however, remains fluid.

SIMILARITY OF *FICUS, CASTILLOA,* AND *FUNTUMIA* LATICES

Microscopically examined, the latex is seen to consist of spherical drops. Obviously the hydrocarbon in the latex is a fluid. The same applies to *Castilloa elastica* latex from Mexico, also cultivated at one time on a considerable scale.

This latex creams even more rapidly than *Ficus*, and when preserved in a bottle, partial agglomeration of the cream takes place in a manner similar to *Ficus*, resulting in an irreversible and irregular shaped lump or clot. Samples dispatched home may arrive in this condition, and it may be that the clotting is similar to that produced by the churning of milk. Acids have no coagulating effect either on *Castilloa* or *Ficus*, or likewise *Funtumia* or other latices I have come across.

Daniel, in the publication already referred to, deals at some length with the reason for the non-coagulation of *Ficus elastica* latex with acids and suggests the presence of a natural stabilizer. It might, however, be due to the positive charge on the particles, although in that case the addition of alkalies such as the ammonia would cause coagulation. It will be recalled that the latex examined by Daniel was made alkaline with ammonia before dispatch. The cause of the stability or instability of latices is at present but little understood; thus the effect of the cationic soaps such as cetylpyridinium bromide on preserved *Hevea* latex is unexpected. This substance in sufficient quantity reverses the charge on the particles, but small quantities will coagulate preserved *Hevea* latex although insufficient to neutralize the ammonia present. Unfortunately so little work has been done with latices such as that of *Ficus elastica* that there is no record whether the charge on the particles of the fresh latex is positive or negative.

SEPARATION OF RUBBER FROM *FICUS* LATEX

Ficus rubber is readily obtained by evaporation of the latex. This may be subjected to a preliminary purification by creaming, which is greatly facilitated by the addition of two or three times its own volume of water. Heating the latex promotes agglomeration, *i.e.*, adhesion of some of the particles with one another to form irreversible irregular-shaped clots.

Alternately the latex may be coagulated by a polar solvent such as alcohol of sufficient concentration (rectified spirits). The coagulant effect is immediate and probably due to dehydration, as less concentrated alcohol is without effect. A higher concentration of alcohol is required to coagulate *Ficus* than *Hevea* latex. It is not possible to adjust the proportion of alcohol to obtain a uniform coagulum on mixing, as coagulation is instantaneous when the alcohol comes in contact with the latex. I am, of course, referring to fresh latex as used on the estate; the imported ammonia-treated latex may have behaved differently. It was unfortunate that acting under the impression that *Hevea* latex is typical of rubber latices, ammonia was added to the *Ficus* latex. The ammonia, as Daniel points out, has almost certainly reacted with the "resins", and the nature of the latex has in consequence been considerably altered. Further the latex was obtained at a single first tapping, and for this reason would also be abnormal. Here the conclusions drawn by these authors as to the nature of *Ficus* latex are open to question, and the experiments require repetition with latex obtained from several tappings and dispatched without ammonia treatment.

The use of ammonia as a preservative for *Hevea* latex was not introduced till some time after the date of my experiments, and I have no record of the behavior of *Ficus* latex to this reagent. That *Ficus* latex contains any component which prevents the coagulation of *Hevea* latex is very unlikely, seeing that the former may be coagulated by acetic acid in the ordinary way if first mixed with a small proportion of *Hevea* latex. To obtain rapid and successful coagulation, as with *Hevea* latex alone, the proportion of the latter should be about one-fifth. Smaller proportions, as one-tenth or even one-twentieth, are effective, although coagulation is delayed. The acid serum from the tank in which *Hevea* latex

has been coagulated does not coagulate *Ficus* latex, or not immediately. This would indicate that *Ficus* globules are carried down mechanically when a mixture of the two latices are coagulated with acid.

PROPERTIES OF *FICUS* LATEX

Ficus latex is chalky white in contrast to the slightly cream or "off-color" of *Hevea* latex. The scrap dries down on the trees to a pink hue, and the pared surface of the wood also turns pink. If *Ficus* latex be left to stand exposed to the air in a porcelain dish, creaming and evaporation cause the surface particles to be compacted and a coherent film is formed. Concurrently the surface becomes darker, while underneath the latex is lighter in color, indicating that air is necessary to promote discoloration.

At one time a *Ficus* rubber in crepe form, clean and well prepared, was available on the market, but this rubber was always tinged a shade of dull pink. It is reasonable to suppose that this discoloration is of a similar character to that noted with *Hevea* latex, although the latter tends to a brown rather than a pink color. When *Hevea* plantation rubber was first produced by coagulating latex with a little acetic acid in soup plates to make the so-called Ceylon biscuits, these were dark drown. The pale shade of unsmoked plantation rubber today is the result of care taken to prevent the darkening of the surface of the coagulum by the oxidase naturally present in the latex. This result is obtained by destroying or inhibiting the action of the oxidase by means of a small quantity, say one-third to one-fifth of 1%, of sodium bisulfite added to the latex at as early a stage as possible.

Fresh *Ficus* latex has a faintly acid reaction (to neutral limits). The acidity increases with keeping. Thus I found that 100 cc. of fresh *Ficus* latex required 4 cc. 0.1*N* NaOH for neutralization, judged by color change in the presence of phenolphthalein, whereas after five days, preserved in a stoppered bottle, it required 45 cc. That is, the acidity had increased tenfold; but there was no sign of coagulation. *Ficus* latex has a sweet smell, which becomes more pronounced on keeping. As the latex contains serum components of great variety which might be expected to form suitable food for microorganisms, it would seem that there must be present a powerfully antiseptic and stabilizing component unless the globules are positively charged. On the other hand the increase in acidity is presumably mainly due to lactic acid bacteria, as in the case of *Hevea* latex.

STABILITY OF *FICUS* LATEX

No doubt misled by the report that *Ficus* latex is thick and partly coagulated when it exudes from the tree, Daniel concludes that it develops stability on keeping, and devotes some space to the consideration of the "increase in stability." I have shown *Ficus* latex is stable from the start. It may increase in stability with time, but there is no evidence either way. Any thickening during collection is due to extraneous and probably accidental factors which we have not sufficient data to assess definitely. I suggest, however, that it may be caused by substances allied to tannic acid present on the surface of the bark. I often noticed a similar phenomenon with *Hevea* latex, particularly on wet mornings when the surface of the bark was damp. The clotting or thickening with *Hevea* was similar to that which could be produced by adding a little tannic acid solution to fresh latex. (Tannic acid does not, by itself, form a compact coagulum with fresh *Hevea* latex.)

To avoid misunderstanding it is necessary to make clear the distinction between the clotting or thickening of latex and coagulation. Clotting or thickening is a form of partial and incomplete coagulation. It is seldom if ever met with in preserved latex, but is common with natural latex. It is observed when fresh latex coagulates spontaneously. The coagulation is seldom complete. The fluid at one stage has the appearance of curdled or clotted milk. There are lumps of coagulum which, when squeezed, exude uncoagulated latex. The lumps or clots are of varying size; serum may separate in places. Similarly the addition of tannic acid causes a thickening and curdling, although no compact coagulum is formed and acid is necessary to recover the rubber.

On the other hand coagulation is generally a gradual process. The whole of the latex sets uniformly to a junket-like mass. This is exactly what happens when latex is coagulated on plantations. The whole gradually sets like a jelly. For this reason a parallel phenomenon with preserved latex is the setting of heat-sensitized latex, as for instance in the Kaysam process, which is sometimes described as the gelling of latex. Occasionally in the literature one meets with the expression "a clear coagulation" which betokens a coagulation that is complete without a residue of uncoagulated particles or small clots.

T.S. AND D.R.C. OF *FICUS* AND *HEVEA* LATICES

I made a number of determinations of the total solids in *Ficus* latex. Values obtained for the first two or three tappings were slightly in excess of 40%. Figures actually recorded were 40.7%, 40.6% and 40.3%, with specific gravity 0.975, 0.974 and 0.974. Thus the gravity is very similar to that of a *Hevea* latex of similar total solids capacity. The latex was obtained from about a dozen trees.

Unfortunately I have no record of figures for both total solids and dry rubber content determined on the same sample of *Ficus* latex, but I have two figures for the dry rubber content of other specimens of *Ficus* latex. Two liters of each were coagulated on both occasions with methylated spirits. The coagula were washed, creped and vacuum-dried at a raised temperature. The yields on the two specimens of latex were close, being 27.0% and 26.3%, respectively. If these figures be taken in conjunction with those for total solids, we have T.S. less D.R.C. approximately=13%. That is to say, the dry solids in the latex consist of approximately 67.5% rubber and 32.5% non-rubber hydrocarbons which are removed in the alcoholic serum.

These figures may be compared with parallel ones for *Hevea* latex. Thus a latex having a T.S. of 41.94 gave a D.R.C. of 38.46 with the difference of 3.48, or 91.7% rubber and 8.3% non-rubber hydrocarbons, remaining or removed in the serum. (The rubber in both cases contains "resins," etc., so that the amount of rubber hydrocarbon is of course less.) As already pointed out, the specific gravity is of the same order for *Ficus* as for *Hevea*. This is difficult to harmonize with the much larger proportion of serum-soluble solids in the *Ficus*. *Abiarana* latex with T.S. 37.1% contains gutta 31.2%, or 84.1% gutta hydrocarbon on T.S.; whereas the *Hevea* sample gave rather more.

COHERENCE OF LATEX PARTICLES

Daniel and the others give a table in which they compare the behavior of latices from *Hevea, Abiarana, Ficus* and *Jelutong*. I have already pointed out the error respecting the stability of *Ficus* latex which is set out in the top row. The fourth column under the heading, "Behavior under the Influence of an

Electric Current," calls for comment. It is stated, regarding *Hevea* latex, that as a distinguishing characteristic the particles form a coherent skin, but this depends on the conditions of the experiment. Thus on reversing the current the particles are loosened and move away toward the other electrode which has now been made the anode[6]. This could not take place if the particles had united to form a coherent skin, although after a time the deposit is said to become sufficiently coherent to be washed clean with a stream of water. Again the particles under certain circumstances are so loosely aggregated that they rise to the surface as a cream. This is, in fact, the principle of the electrodecantation process for concentrating latex[7]. Or again in recent work by Rowe and myself[8] on pressure dialysis it has been noted that the cream freshly formed on the membrane could be redispersed without difficulty, but after some time tends to become denser and less easily dispersed. In fact the coherence between the deposited particles varies with the conditions, although it may be that *Hevea* particles cohere more readily than those of other latices.

I remember a particularly striking example regarding *Castilloa* latex. At the Rubber Exhibition in London in 1908 centrifugal machines were exhibited for separating rubber as a cream from this latex. They were relatively slow-speed machines, consisting of an annular space for the latex formed by the inner surface of a drum and the outer surface of an inner cylinder, a cotton cloth being wrapped around the outer surface of the inner cylinder on which the latex particles were deposited. I took away with me a piece of this cloth with the deposit of latex cream upon it. When hung in air it was dry in a few hours, although perhaps ¼-inch thick. If, however, the deposit of cream were gently pressed with the fingers before hanging, drying took some days instead of hours. It would seem that the *Castilloa* globules were so lightly compacted in the directly deposited cream that the moisture between them could readily evaporate from the interstices of presumably what was a porous structure, whereas, after compressing, the water was locked into the wet mass and could only evaporate by slow diffusion through the rubber itself.

Incidentally it would be interesting to discover how far the coherence of deposited particles, whether deposited electrically or mechanically, is to be regarded as a coagulation in the usual sense of the word. It cannot be a coagulation as ordinarily understood if produced mechanically, for there is no electrolyte or coagulating ion present. It has, however, been assumed that when latex is subjected to an electric current, the positively charged ions migrate from the anode surface under the influence of the electric potential and, meeting the negatively charged ions, cause coagulation[9]. But if this were the case, reversibility of the deposited particles by altering the direction of the current would not be possible, as the particles would be already in contact with and adherent to each other and the anode surface. Or would it be possible to separate the particles as a cream electrophoretically. If the particles were actually coagulated on the surface of the anode by the action of the liberated ions, then we have a simple explanation of the difference between *Hevea* and *Ficus* latices, as the former is and the latter is not, coagulable by electrolytes. As it stands, the most that can be said is that the particles are at first deposited loosely, but that as the action continues, those first deposited and nearest the anode surface become compacted and are no longer removable by mechanical or electrical means. This gradual coherence of the particles may be caused merely by close mechanical contact or by an electrical discharge, but in the latter case there is no explanation of the delay. Coagulation by the ions on discharge at the surface of the electrode would be instantaneous.

CREAMING OF *FICUS* LATEX

Under "Density of Particles and Coagulum,"[3] it is stated that *Ficus* latex particles are fractionated to a lighter and heavier layer. This may have been the case with the ammonia-treated latex with which the authors worked, but I have no note of any such separation with fresh untreated *Ficus* latex. As stated, this latex creams fairly readily, though not so readily as *Castilloa* latex. When diluted with water, it creams very readily, yielding only two layers, an upper layer of cream and an under layer substantially clear.

CAUSE OF PINK COLORATION

The authors also suggest the pink color is due to alkaline decomposition of sugars[3]. Having regard to the fact that the color deepens on exposure to air and particularly in the presence of weak acid and becomes very dark in a few days, it would seem much more likely that it is due to an oxidase or peroxidase such as is found in *Hevea* latex and in a very large number of vegetable tissues, as that of the apple and the fleshy coverings of walnuts.

NOTES ON *CASTILLOA* LATEX

My notebook also contains a few rough observations regarding *Castilloa* latex, and it may be worth while to put them on record. This latex is strongly acid as it exudes from the tree, rapidly creaming to give a light-brown cream and a dark-brown serum. The latex is conveniently purified by diluting the cream with water and recreaming. Six grams of fresh latex required approximately 6 cc. 0.1*N* NaOH to neutralize as judged by the change in color. The T.S. of this latex was 37.3%. Like *Ficus*, it is not coagulable with acids, but with alcohol, and it does not putrefy. I attempted to treatment with ether to repeat the experiment made on this latex by the late C. O. Weber in Mexico. It will be remembered he obtained a mobile ethereal solution of the rubber which suddenly polymerized to yield a stiff gell, leading him to the conclusion that the rubber in the latex was present in a simpler form than when recovered by the ordinary processes. I failed to obtain the mobile liquid. The effect of ether was to cause coagulation exactly as with fresh *Hevea* or *Ficus*. Subsequently the hydrocarbon dissolved to form a very thick yellow fimbriated gell, with a dark-brown serum below. A repetition of the experiments allowing the latex to drip into the ether straight from the tree gave a similar result.

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THE PROPERTIES OF RUBBER PREPARED FROM DIALYZED LATEX *

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PART I

Preparation of Rubbers

Rubber articles are prepared from ammonia-preserved latex by two principal processes, *viz.*, evaporation or coagulation, or by a combination of both. The object of this work was to determine what advantages are to be obtained by the use of a latex purified by dialysis. An 8-gallon batch of normal ammonia-preserved latex (from *Hevea brasiliensis*) was available and all the rubbers were prepared from this batch unless otherwise stated. The latex was kept for several days and decanted from the sludge which settles out. After straining, it was stored in one-gallon cans until required for use.

Some of the latex was dialyzed through membranes of regenerated cellulose in the apparatus previously described by the authors[1]. Some aqueous ammonia was added to the latex daily to preserve stability, and three charges of distilled water were used to complete the purification. A pressure was applied to the latex and adjusted to allow slight dilution so that there was no formation of paste on the membranes. The latex was analyzed, before and after dialysis, for total solids and dry rubber content. The former were determined by evaporating a weighed portion of the latex to constant weight at 70°. The dry rubber content was determined by coagulating the latex with about an equal volume of 1% acetic acid, crepeing the coagulum on a washing machine, and drying the crepe at 70°.

The reserved batch of latex had the following analysis:

Latex	Total solids % (t)	Dry rubber content % (d)	Excess of t over d as % of d
Normal	44.1	40.6	8.6
Dialyzed	34.2	34.2	0

Thus the whole difference between the total solids and dry rubber content figures of the latex was removed by dialysis. This observation has been confirmed in other dialyses of latex. As will be shown in Part II, the nitrogen and ash contents of crepe from ammonia-preserved latex are only a trifle higher than in crepe from the same latex after dialysis. Acetic acid therefore coagulates substantially the whole of the colloidal, non-diffusible contents of the latex. In confirmation of this, the diffusible contents of the serum, which are removable by dialysis, show only a trace of precipitate when the serum is acidified.

Four rubbers were prepared for tests, *viz.*, two crepes from the acetic acid coagulation of the undialyzed and dialyzed latex and two whole rubbers by the evaporation of these latices in trays at room temperature. These latter were dry-creped to facilitate drying.

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A batch of the crepe from the dialyzed latex was extracted with acetone in a large extractor of the solvent reflux type. A portion was retained for comparison of its vulcanizing and aging characteristics. The extraction was not complete, the extracted rubber having an acetone extract of 1.3%.

Curing Characteristics

The rubbers were vulcanized in a six-ring mould, which was heated in boiling water. By this means accurate repeat cures can be obtained with simple apparatus, as the conditions are more easily kept constant and reproducible. The uniformity to be obtained by this method is illustrated in Table I, where the

Table I

Whole-Latex Rubber Cured for 3 Hours at 100°

Cure no.	*E*.120	TSB	EB %
37	568	259	758
38	585	253	756
39	590	238	748
40	582	241	735
41	575	247	738
Mean	585	248	747

E.120 = % extension at a load of 120 kg. per sq. cm.
TSB = Tensile strength at break, kg. per sq. cm.
EB% = % elongation at break.

stress-strain data obtained on a Schopper tester are given for five repeat-vulcanizations on the same batch of whole-latex rubber from undialyzed latex.

The rubbers were compounded as follows: rubber 100, sulfur 2.5, zinc oxide 6, stearic acid 1, mercaptobenzothiazole 1. In the case of the whole-latex rubber from the undialyzed latex, 109 parts were taken to allow for the serum solids. The rubbers were milled on a laboratory mill at 65° to the same consistency, judged by their appearance and working on the mill. The compounding ingredients were then added according to an established routine. The stock was sheeted and kept between Cellophane sheets until required. The same operator carried out all the mixings. A commercial blanket crepe was included for comparison.

The consistency of the compounded stock was checked with a Cusson durometer and found to be substantially uniform. With this technique but little difference was found in the rate of breakdown of the rubbers; they were softened in 10-12 minutes and the batches completed in 24-28 minutes. The acetone-extracted crepe from the dialyzed latex was, however, in four millings slightly quicker in softening than the other rubbers. This is consistent with the view that softening on milling is partly an oxidation effect, since acetone is known to extract natural antioxidants from the rubber[2]. The whole-latex rubbers might have been expected to be slower softening, but they had already been partly broken down when being creped to facilitate drying.

After curing, the rings were kept for one day at room temperature before testing. The stress-strain curves were obtained autographically. The average tensile strength at break was calculated from the values for the six rings by the method of Davies and Horrobin[3], which gives the most probable value. The extensibility may be used as an index of the degree of curing and in this work was taken as the elongation % at a stress of 120 kg. per sq. cm. (*E*. 120) and measured from the stress-strain curves.

The results obtained are shown graphically in Figs. 1 and 2. The curves represent: (*a*) A commercial blanket crepe. (*b*) Crepe from coagulated ammonia-preserved latex. (*c*) Crepe from coagulated dialyzed ammonia-preserved latex. (*d*) As (*c*), acetone-extracted. (*e*) Whole-latex rubber from ammonia-preserved latex. (*f*) Whole-latex rubber from dialyzed ammonia-preserved latex. (*g*) Blanket crepe (*a*) plus 0.2% of diphenylguanidine. (*h*) Crepe (*c*) from dialyzed latex, plus 0.4% of diphenylguanidine.

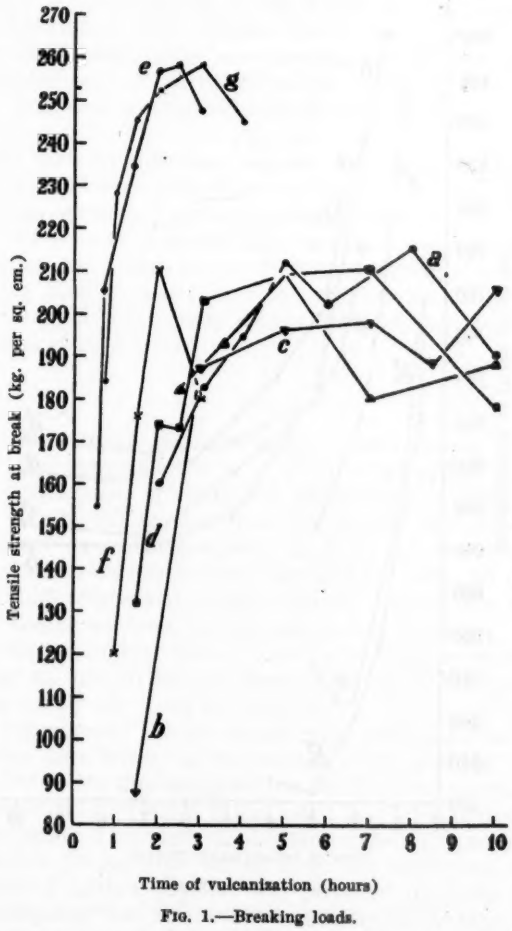

FIG. 1.—Breaking loads.

It will be seen from the graphs that all the crepes (*a*)-(*d*) have similar vulcanizing characteristics, although the commercial blanket crepe (*a*) (prepared, of course, from a fresh and different batch of latex) is somewhat slower vulcanizing. The whole-latex rubber (*e*) is much faster vulcanizing and has a greater maximum strength. The whole-latex rubber from the dialyzed latex (*f*) is intermediate in rate of vulcanizing, but has no greater maximum strength than the crepes. Hence dialysis removes only a part of the natural accelerator present

in the serum. In other words, part of the natural accelerator is crystalloidal and part colloidal in respect to the dialyzing membrane used. Of the colloidal part, a part again is acid-soluble as the crepe from coagulated dialyzed latex vulcanizes more slowly than the total rubber from the same.

The values for tensile strength of the crepes do not agree exactly, but it can be shown that the differences are not significant. It is known that, in spite of uniformity in procedure, variations occur in the values for tensile strength at

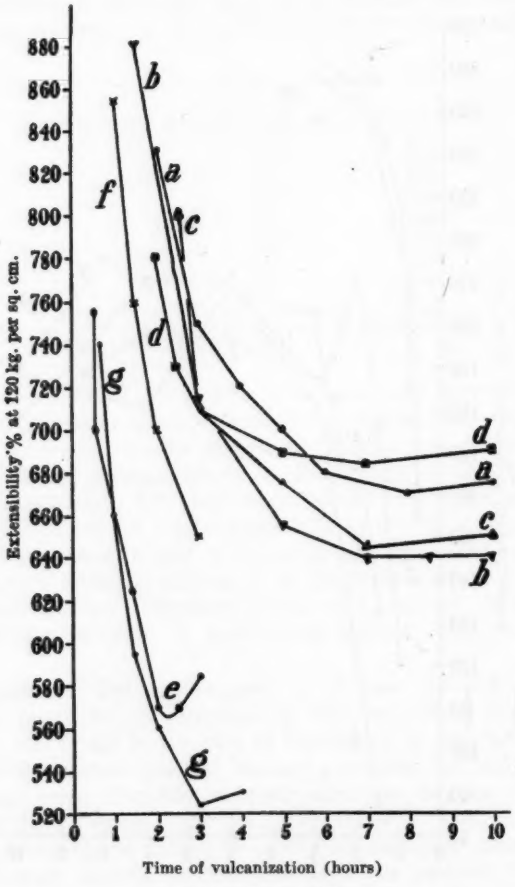

FIG. 2.—Extensibility.

break, and that these variations are distributed about a mean according to the laws of probability[3]. The standard error (s) for a single test was therefore calculated from the data obtained in testing 240 rings of this series by the method of Pearson and Davies[4] and found to be 11.8 kg. per sq. cm. The tensile strength figures recorded for the crepes are the means of (on the average) four rings of a set. The standard error of the difference between two means= $s\sqrt{[(1/n_1)+(1/n_2)]}$ (where n_1 and n_2 are the number of tests in a set) or 16.5 kg. per sq. cm. To be significant a difference must therefore be greater

than $2 \times 16.5 = 33$ kg. per sq. cm. It will be seen that the differences between the strengths of the crepe do not exceed this, so they are not significant. That is to say, they fall within the range of variation that might be expected if the same rubber had been used in each case.

The greater strength and more rapid vulcanizing of the whole-latex rubber from ammonia-preserved latex is probably due to some dialyzable accelerator in the serum having a "boosting" effect on the mercaptobenzothiazole accelerator. Confirmation of this view was obtained by adding 0.2% of diphenylguanidine to the blanket crepe (*g*). This increased the rate of vulcanizing and strength of the vulcanizate, as shown in Figs. 1 and 2 (*g*), to values very close to those for the whole-latex rubber. It is already known that some of the serum components have an accelerating effect on vulcanization[5]. It may be that they are of a basic nature, derived from partial hydrolysis of the proteins in the ammonia-preserved latex. This view is consistent with the activating effect of the guanidine described above.

Dawson[5] found that the difference between whole-latex rubber and crepe in rate of vulcanizing was lost on adding an accelerator. The considerable difference reported here under somewhat similar conditions may be due to the fact that this whole-latex rubber was prepared from ammonia-preserved latex, since it is known that ammonia has a considerable effect on a number of latex constituents[6]. However, all latex used in manufacturing processes has been preserved with ammonia for some time before being used, so that the effects described are of interest to all users of such latex.

Aging of Vulcanizates

The deterioration in tensile strength of the vulcanizates on heating in air in an oven at 70° has been adopted as a criterion of aging, and a degree of vulcanizing has been chosen at which the extensibility is 700% for a load of 120 kg. per sq. cm. It will be seen from Fig. 2 that this stage is reached in 5 hours' vulcanizing for the blanket crepe, 3½ hours for the other three crepes, 2 hours for the whole-latex rubber from the dialyzed latex, 50 minutes for the blanket crepe + 0.2% diphenylguanidine, and 40 minutes for the whole-latex rubber from the undialyzed latex. It will also be seen from Fig. 1 that at these times of curing all the rubbers have developed a tensile strength at break of about 200 kg. per sq. cm., so that at these times two of the properties of the rubbers are substantially the same for them all.

For the aging experiments, the laboratory crepe prepared from the ammonia-preserved latex was used, instead of the blanket crepe, on which to demonstrate the "boosting" effect of the diphenylguanidine on the mercaptobenzothiazole. To get the same stress-strain properties, it was found that 0.4% of diphenylguanidine was necessary instead of 0.2% with the blanket crepe. The whole of the batch of whole-latex rubber prepared by drying down the undialyzed latex had been used, and therefore a further quantity was prepared from the same batch of latex. It was anticipated that this would be similar to the first batch. It was found, however, that this second batch had to be vulcanized for 70 minutes, instead of 40 minutes, to obtain the same extensibility. The slower rate of vulcanizing is presumably due to some change in the non-rubber components of the latex during storage. The effect of ammonia-preservation of latex on the rate of vulcanization of the rubber has been reported[7]. It was found that there is a drop in the rate of vulcanization within one day, followed by a rise for two months and then a gradual fall. Presumably the batch of latex in use

in the above experiments is in the range of gradual fall. The batches actually used for the aging experiments were therefore vulcanized for the times shown in Table II, which also shows the stress-strain data obtained from one set of rings. The other sets of rings were similarly vulcanized and used for aging.

TABLE II

RUBBERS FOR AGING EXPERIMENTS

Rubber	Cure at 100°	Extensibility E. 120	TSB kg. per sq. cm.	EB%
(*a*)	5 hours	695	186	790
(*b*)	3½ hours	685	202	796
(*c*)	3½ hours	725	193	830
(*d*)	3½ hours	700	187	801
(*f*)	2 hours	720	199	825
(*e*)	70 minutes	700	195	811
(*h*)	50 minutes	695	207	810

After the rings for the aging experiments had been vulcanized, they were handled as quickly as possible in diffused light and then stored in the dark for at least a week before starting aging. This precaution avoids the activating effect of light on heat-aging which may persist for some time after exposure to light[8]. The results are shown graphically in Fig. 3.

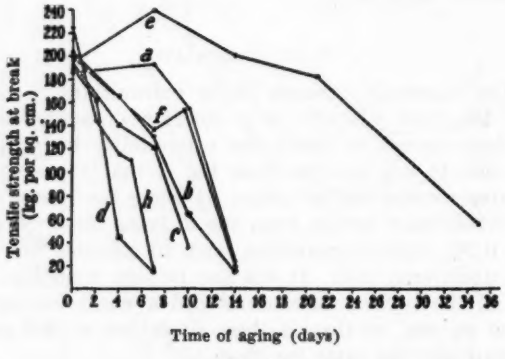

FIG. 3.

If the number of days required for the strength to fall to 100 kg. per sq. cm. is taken as an indication of resistance to aging, the rubbers can be arranged as follows in order of increasing aging-resistance (expressed in days): (*d*) 3; (*h*) 5; (*c*) 8; (*b*) 8; (*f*) 11½; (*a*) 11½; (*e*) 30. A comparison of (*c*) and (*b*) shows that dialysis has made no difference to the aging properties of the crepes. This might be expected, since coagulation and crepeing leaves in the serum substantially all the water-soluble ingredients that are removable by dialysis. In comparison with a commercial crepe, prepared, of course, from fresh latex, the aging is not quite so good. This effect was also noticed in some preliminary tests on another batch of ammonia-preserved latex, in comparison with another commercial crepe but using a different formula. This would suggest that the changes which occur during ammonia preservation have an adverse effect on the aging of the crepes. Acetone extraction of the crepe (*d*) gives much poorer

aging, as is to be expected, since the acetone extract is known to contain antioxidants.

A comparison of (*f*) with (*c*) shows that the whole-latex rubber from dialyzed latex ages better than the crepe, and a comparison with (*e*) shows very much better aging for the whole-latex rubber from undialyzed latex. This indicates that there are very effective antioxidants in the dialyzable serum solids of the ammonia-preserved latex. A water-soluble antioxidant has been reported[2] in the acetone extract of crepe rubber, and sprayed latex rubber has been found to have somewhat better aging properties than other forms[9]. It might be said against this view that the whole-latex rubber from the undialyzed latex reaches a higher tensile strength on curing than the crepes (Fig. 1), and that this rise in strength, which might occur by after-vulcanization during aging, would counteract deterioration due to oxidation. A comparison, however, of the crepe plus diphenylguanidine (*h*) with the whole-latex rubber (*e*) shows that, although they have similar vulcanizing characteristics, the latter has much better aging properties. This better aging can, therefore, only be ascribed to dialyzable components of latex serum. Therefore the latex contains at least two antioxidants, one dialyzable, the other water-insoluble but acetone-soluble.

Acetone Extracts

The acetone extracts of the four rubbers were determined in the absence of light. The rubbers were milled thin and completely wrapped in extracted black filter-paper and the extractor was shielded from direct sunlight. The extractor was of the A.S.T.M. type with glass thimbles. If the extraction is not carried out in the dark the extract continues to increase indefinitely with time[10]. The extractions are complete in about 40 hours. The values obtained were: (*c*) 2.91%; (*b*) 3.30%; (*f*) 3.26%; (*e*) 7.42%. Dialysis has reduced the acetone-soluble components of both the crepe and the whole rubber. A portion of the acetone extract of normal rubbers is water-soluble, and it is presumably this fraction which is reduced by dialysis of the latex.

DISCUSSION

The principal advantage to be expected from the use of dialyzed latex is a lower water absorption for the whole-latex rubbers, such as are obtained in dipping processes. The water absorptions are described in Part II. It is necessary, however, to determine what effect, detrimental or otherwise, dialysis has on vulcanizing and aging characteristics. It will be seen from the results given above that dialysis has a considerable effect on the properties of the whole-latex rubber. Dialysis removes from the latex, and therefore from the whole-latex rubber, an accelerator and an antioxidant, so that the rubbers from the dialyzed latex do not vulcanize so rapidly nor do they age so well as the whole rubbers. They behave similarly to crepe rubber. The deterioration in aging-resistance is most marked, and it may therefore be necessary in certain cases to give extra anti-aging protection to rubbers from dialyzed latex. The properties of the crepes from either dialyzed or undialyzed latex are, however, similar, so that when rubbers are prepared by coagulation processes, no appreciable difference may be expected.

PART II

This deals with the effect of dialysis of latex on water absorption of the rubbers, and in order to assess the relative effect of dialysis in comparison with

other processes the dialyzed latex has been further purified by the methods described below. Crepes and whole-latex rubbers were prepared and the water absorptions, nitrogen and ash contents determined for them all.

A portion, diluted to 20% was concentrated in a laboratory centrifuge[11], giving a cream of 62.5% and a skim of 6.5%. A portion was creamed by the Pauli electric process[12]. This has the advantage over the centrifugal process in giving complete creaming, the separated serum being free from rubber. It also has the advantage over other creaming processes in that no creaming agents need be added. The dialyzed latex was diluted to 15% and creamed to about 50%. A portion of this was further treated twice more by the same process, so that the final latex had been thrice creamed. Another portion of dialyzed latex was heated at 70° in sealed bottles with an equal volume of 4% caustic soda solution, one for 65 hours and the other for 180 hours[13]. The treated latices were thoroughly dialyzed to remove caustic soda and protein hydrolysis products, coagulated with acetic acid and creped. The rubbers obtained were inclined to be tacky, but kept quite well in the dark. For comparison, rubbers from a commercial 60% centrifugally concentrated latex and a commercial low-nitrogen rubber were included.

Water Absorption, Nitrogen and Ash

The rubbers were cut into fine shreds and exposed in flat glass dishes in vacuum desiccators in a water tank maintained at 25° ± 0.5° C. The rubbers were first dried at 0% R.H. over concentrated sulfuric acid and then allowed to absorb moisture at 75% R.H. over a saturated solution of sodium chloride containing excess of salt. Finally they were dried again to check whether any oxidation had occurred during the experiment. To minimize the possibility of oxidation the desiccators were evacuated. When the samples were removed for weighing, the dishes were covered with a tared watch glass. Equilibrium was usually reached in two to three days. Absorption was determined from the vapor rather than the liquid as the latter method leads to results vitiated by the leaching out of some of the water-soluble components. 75% R.H. was chosen instead of 100% R.H. because equilibrium is reached more quickly. At 100% R.H. it is doubtful whether equilibrium is ever reached[14]. The equilibrium absorption from the vapor is the same as from a solution of the same vapor pressure[15].

The nitrogen content was determined by the Kjeldahl method, accelerated by the addition of a little copper sulfate and selenious acid. During distillation of the ammonia, a stream of ammonia-free air was drawn through the apparatus. The percentage of ash was determined in a platinum crucible without allowing the rubber to catch fire. The results are given in Table III.

DISCUSSION

A comparison of the whole-latex rubber from ammonia-preserved latex (*e*) with the whole-latex rubber from dialyzed latex (*f*) shows the large reduction effected by dialysis in the water absorption of the whole-latex rubbers. There is a considerable reduction in ash, showing, as might be expected, removal of most of the inorganic salts. The nitrogen is also lower, indicating that the nitrogen is not all present as protein. The removal of part of the nitrogen by dialysis has already been reported[16]. The figures also indicate that the dialyzable serum solids enormously increase water absorption, but after their removal further improvement is obtainable only by reduction in the nitrogen.

The comparison of (*b*) and (*c*), the crepes from latex before and after dialysis, shows only a slight advantage in favor of the crepe from dialyzed latex. This indicates that coagulation and washing removes substantially the same impurities as dialysis, and that dialysis alone will not produce a purer rubber than coagulation and washing.

(*d*) shows that acetone extraction gives a slightly lower water absorption. It also removes a little nitrogen. This was confirmed by an analysis of the extract, which contained 0.7% N.

A comparison of the whole-latex rubber from dialyzed latex (*f*) with the crepes shows the former to have only a slightly higher water absorption, nitrogen and ash, indicating that a dialyzed latex is approximately an aqueous dispersion of a crepe, from this point of view. On comparing (*f*) with (*b*), (*f*) shows

TABLE III

Rubber	Water abs. %	% N	% ash
(*a*) Commercial blanket crepe	0.41	0.38	0.19
(*b*) Crepe from coagulated ammonia-preserved latex	0.29	0.31	0.23
(*c*) Crepe from coagulated dialyzed ammonia-preserved latex	0.27	0.27	0.18
(*d*) No. (*c*) acetone-extracted	0.20	0.24	0.22
(*e*) Whole-latex rubber from ammonia-preserved latex	2.87	0.44	0.94
(*f*) Whole-latex rubber from dialyzed ammonia-preserved latex	0.41	0.37	0.29
(*k*) Centrifuge cream, whole-cream rubber	0.17	0.11	0.06
(*l*) Centrifuge cream coagulated and creped	0.09	0.09	0.13
(*m*) Electrical process once creamed, whole-cream rubber	0.26	0.17	0.14
(*n*) Electrical process once creamed, and creped	0.21	0.13	0.08
(*p*) Electrical process thrice creamed, whole-cream rubber	0.18	0.12	0.09
(*r*) Electrical process thrice creamed and creped	0.17	0.10	0.06
(*s*) Alkali treatment, 65 hours, crepe	0.07	0.09	0.14
(*t*) Alkali treatment, 180 hours, crepe	0.08	0.07	0.18
(*u*) Whole-latex rubber from a commercial 60% centrifugally concentrated latex	1.45	0.23	0.56
(*w*) Crepe from commercial 60% centrifugally concentrated latex	0.14	0.20	0.10
(*x*) Commercial low-nitrogen rubber	0.05	0.04	0.13
(*y*) Commercial low-nitrogen rubber with antioxidant	0.12	0.06	0.20

substantially higher figures, indicating that the serum of dialyzed latex still contains a quantity of non-dialyzable impurities.

A comparison of a whole-latex rubber from a commercial 60% centrifugally concentrated latex (*u*) with (*f*) shows that dialysis is a much more effective method of purification than a single-stage concentration by centrifuging, so far as concerns serum solids, but it is not so effective in removing nitrogen.

A comparison of (*k*), (*l*), (*m*), (*n*), (*p*), (*s*) and (*t*), the rubbers from further treatment of the dialyzed latex, shows a substantial further reduction in the water absorption. This is accompanied by a corresponding reduction in the percentage of nitrogen and percentage of ash, indicating that the lower ranges of water absorption can be attained only by the removal of colloidal serum components, which of course largely remain in the skim. The alkali treatment in particular has effected a reduction in water absorption to a stage similar,

but not equal, to that of the commercial low-nitrogen rubbers (*x*) and (*y*). The crepe from a commercial (60%) centrifugally concentrated latex also has a lower water absorption and nitrogen than other crepes, indicating that centrifuging has removed in the skim some of the colloidal serum components which are coagulated by acid in preparing crepes.

The loss of rubber in the skim by the centrifugal process, which in this case amounted to about 20% of the rubber in the original latex, will consist of the smaller particles. Lucas[17] has shown recently that 18% of the mass of rubber in latex contains 92% of the (smaller) particles, so that the rubber surface in the skim will be, relatively to the mass, much greater than in the cream. Therefore impurities adsorbed on the surface will be separated to a greater extent by centrifuging than by complete creaming, as was found to be the case.

The whole-latex rubber from the original latex contains 0.44% of nitrogen. After dialysis of the latex, the value is reduced to 0.37%, *i.e.*, 16% of the nitrogen is in the form of water-soluble diffusible substances in the latex. Beadle and Stevens[16] obtained the figures 19%, 26%, and 21% (average 22%) for three latices in 1912. At that time the system of tapping (herringbone) was more severe than today and this may have had some influence on the composition. After being creamed thrice, the nitrogen is reduced to 0.12%. This probably corresponds closely with the amount of protein strongly sorbed on the particles, since it is not much lower than the value for once-creamed latex, *viz.*, 0.17%. Kemp[18] has also reported a value of 0.108% nitrogen for latex thrice creamed in a De Laval separator. To obtain lower values for nitrogen and for water absorpton, it would appear to be necessary to resort to chemical methods in addition to the above physical methods, assuming that more than thrice repeated creaming is impracticable. (*s*) and (*t*) show the result of alkali treatment of the latex, followed by thorough dialysis. The nitrogen has been still further reduced, with a corresponding reduction in water absorption. This is not altogether in agreement with some results given by Noble[19], who found rather high values for water absorption for rubber obtained by alkali treatment of latex, followed by dialysis. This was probably due to incomplete dialysis, since the ash content was also rather high. Also, in dialysis of the untreated latex only 93% of the diffusible impurities were removed by his apparatus. However, the nitrogen content was reduced to a low figure, so that had dialysis been complete, a low water absorption would also have been obtained. If then 0.12% nitrogen is taken as the amount strongly sorbed on the latex particles, then $0.37\% - 0.12\% = 0.25\%$ nitrogen, or 57%, is present in the serum as colloidal, non-diffusible substances. A proportion of this will be reversibly adsorbed on the latex particles, depending on the concentration of these substances, in the serum, *i.e.*, on the dilution of the latex. The 0.12% nitrogen strongly sorbed is 27% of the total nitrogen. The nitrogen in latex may thus be classified approximately as follows: (1) water-soluble, diffusible, removable by dialysis 16%; (2) colloidally dispersed in serum, removable by creaming 57%; (3) strongly sorbed, removable although not completely by chemical treatment 27%.

Utilization of Dialyzed Latex

From the foregoing data it appears that dialysis, even when carried to completion, does not remove the bulk of the nitrogenous components from the latex as these are colloidal. Consequently rubber from such latex is still too moisture-absorbent for use in specialized electrical work. The process may, however, form a useful preliminary purification.

The process should be found valuable in the manufacture of goods directly from latex. By the nature of the deposition latex processes such as dipping, a large proportion of the dialyzable components is retained in the finished article and may be a source of trouble. Part of these components are hygroscopic and tend to exude on the surface. It is possible to digest freshly prepared articles in warm water to enable these components to diffuse out. When however the article is vulcanized, the diffusion of these crystalloidal ingredients may be very slow, so that only a portion of them is removable in a reasonable time.

The use of creamed latex is a great improvement, as this latex contains much less crystalloid material and is less moisture-absorbent than untreated latex [compare (*u*) and (*e*)]. If, however, the latex be dialyzed, substantially the whole of these crystalloids is removed (*f*) with consequent improvement of the product. Further the physical properties of the latex film are improved by dialysis. The following figures were obtained for tensile tests determined on the bubble-blowing apparatus of Flint and Naunton[20]:

Film from	Kg. per sq. cm.	Extension (normal elongation 100)
Dialyzed latex	48	688
Undialyzed control	26	850

It will be noted that the tensile strength is much higher, although the extension is less. The former more than compensates for the latter, for the tensile products are in the proportion of 3:2.

The authors are indebted to the Board of the British Rubber Producers Research Association for permission to publish the results of these experiments.

AN X-RAY INVESTIGATION OF CRYSTALLINITY IN RUBBER *

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INTRODUCTION

The crystalline structure which rubber exhibits under certain circumstances[1-3] has come to be regarded as associated with a secondary or micellar structure of long chain molecules. The exact mechanism by which the localized ordered regions appear is a speculative subject in recent developments of the micellar theory of long chain polymeric materials. The views of various workers on this subject have been summarized by other authors[4].

The crystalline structure of rubber displays varying degrees and types of orientation of the crystal units, depending on the conditions under which crystallization occurs. The amorphous x-ray diffraction pattern of unstretched rubber is shown in Figure 1, the unoriented crystalline diagram for frozen rubber in Figure 2. When crystallization is induced by stretching, the crystallites are aligned along the axis of stretching, giving the fiber diagrams of Figures 3 and 4. In this case there is random orientation of the other two axes of the crystallites. "Higher orientation," in which all three axes of the crystallites are aligned, gives the diagram of Figure 15 and can be secured with suitable dimensions of the stretched piece.

The combined effect of stretching and freezing rubber was tested by x-ray diffraction shortly after the fact was discovered that rubber gave a fiber diagram upon stretching. Thus, Hauser and Mark[2] stretched a piece of raw rubber to 500 per cent extension, cooled it to $-4°$ C and secured the x-ray diffraction pattern at this temperature. The result of this experiment was negative in that no alteration of the pattern, due to the cooling, was apparent. Hünemörder and Rosbaud[3] obtained a fiber diagram by carefully stretching frozen rubber. Meyer, Susich and Valko also have reported results on the stretching of frozen rubber[5].

More recently, Smith and Saylor[6] have studied a phenomenon which they have termed the secondary increase in length of stretched, chilled rubber. They observed that raw rubber stretched to intermediate elongations increased about four per cent in length when chilled at about 0° C. This effect was explained as due to a movement of the molecules into the crystalline arrangement, the more parallel arrangement resulting in the increase in length, a reasonable and logical explanation. The present authors have found that the x-ray diffraction phenomena which accompany this effect are much more striking than would be anticipated from the relatively small increase in length compared to the elongations usually necessary to give rise to a fiber diagram. The results should have a direct bearing on such questions as to whether the rubber crystallites are brought into being or merely made evident by stretching, whether they grow in size or in number as stretching proceeds and how the intensity and size of the diffraction spots are related to the size, number and perfection of the ordered regions responsible for them.

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As another possible means of securing new information about the crystallization process due to stretching, the work was extended to investigate more systematically than has been done heretofore the conditions under which "higher orientation" or the ordering of all three axes of the crystallites occurs instead of the parallel alignment of only one axis as in the ordinary fiber diagram.

APPARATUS AND METHODS

The x-ray diffraction patterns were obtained with a General Electric X-Ray Diffraction Unit, employing a Philips Metalix copper target tube operated at 35 kv. peak and 27 milliamperes. Nickel foil was used as a filter to remove the CuK_β radiation. Film-specimen distance in all cases, except where noted, was 5 cm. Exposure times were usually two or three hours.

Since the intensity of the diffraction pattern for rubber has been shown to depend on the rate of stretching[3], the rubber samples, described more specifically later, were stretched to the desired elongations by means of a falling weight. This insured comparable and rapid speeds of stretching. The stretched pieces were clamped to aluminum strips and frozen in the freezing compartment of an electric refrigerator, temperature approximately $-5°$ C, for a period of about 18 hours.

To keep a specimen frozen during exposure, a yoke was made from a thick copper bar. The ends of the yoke were immersed in a mixture of acetone and solid carbon dioxide and the exposed surface insulated with asbestos. A hole was drilled in the center of the bar, suitably positioned for containing the sample and closed by a screw. A one-eighth inch diameter hole was drilled at right angles to this to permit the passage of the x-ray beam through the sample. The ends of this hole were covered with Cellophane which was kept free of frost by a trickle of acetone over the surface.

The samples were cut with a scissors from the stretched, frozen strips of rubber immersed in acetone-solid carbon dioxide mixture and could be quickly transferred therefrom to the cavity in the copper bar without thawing.

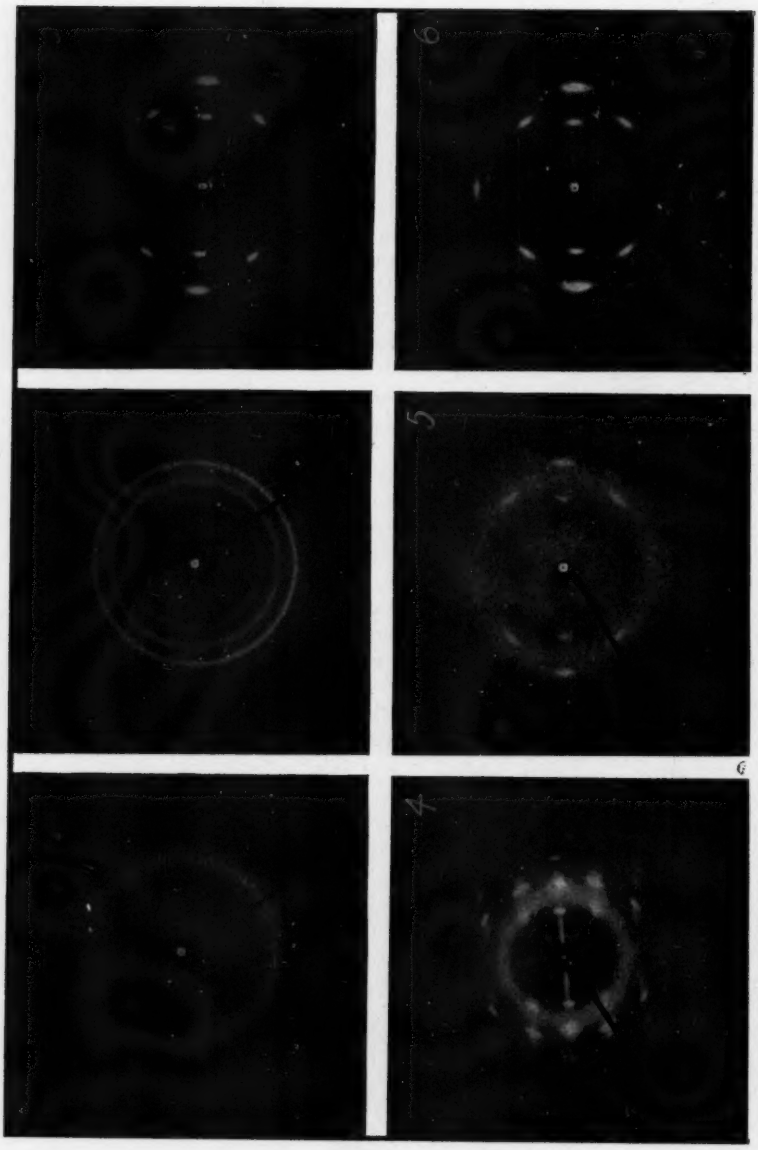
It is now generally known that if raw rubber is suddenly chilled in liquid air or even in an acetone-solid carbon dioxide mixture, it does not give an x-ray diffraction pattern of crystalline material, but an amorphous halo[7]. To secure the Debye-Scherrer rings of Figure 2, cooling at a moderately low temperature over a period of time is required. After the rubber is frozen in this fashion, it can be chilled at lower temperatures, as in the technique just described, without materially affecting the x-ray diffraction pattern.

In the study of "higher orientation" in stretched samples, the photometric measurements of the density of the diffraction spots were made with a Zeiss spectrum line photometer.

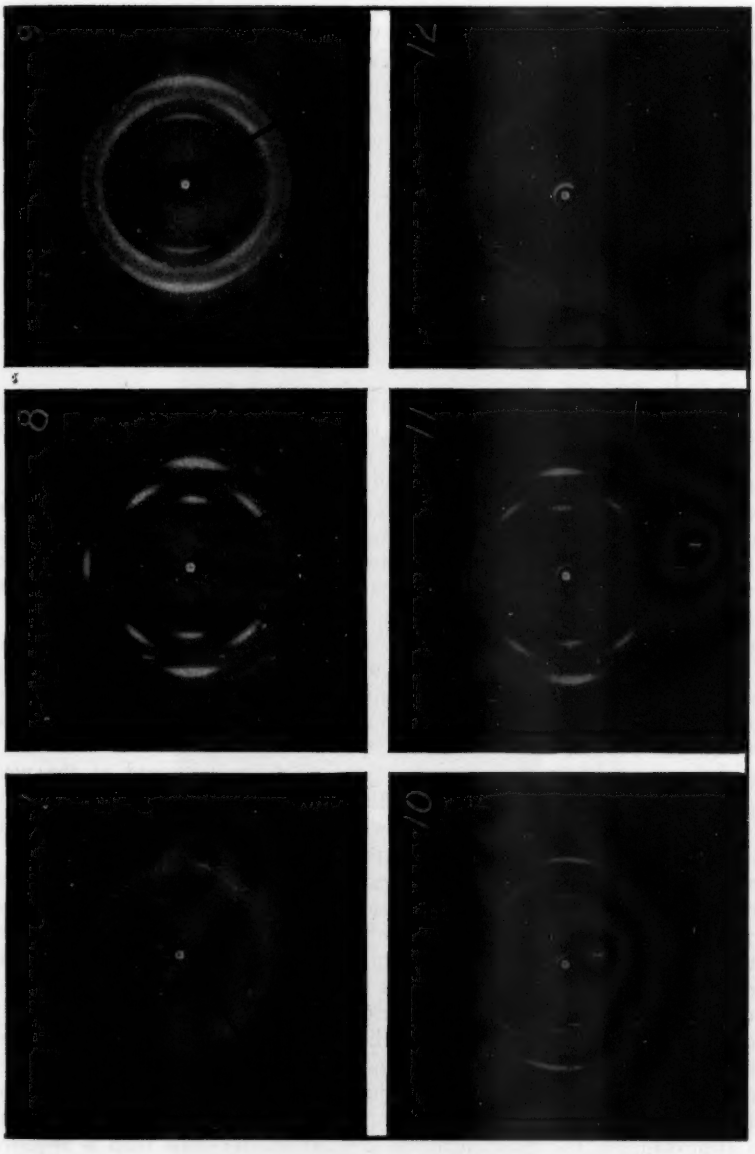
RESULTS

X-ray Diffraction Effects Due to Stretching and Freezing

Figure 5 is the diagram secured for a sample of pale crepe rubber stretched to 350 per cent elongation, taken at room temperature. Figure 6 is the diagram for this identical sample when frozen. The amorphous halo has practically disappeared and the diffraction spots are very intense. There is no trace of the Debye-Scherrer rings of Figure 2. The localized ordered regions or crystallites caused by the stretching act, to all appearances, like nuclei for crystallization when freezing occurs. Figures 7 and 8 demonstrate the effect for an elongation



FIGS. 1-6.—(1) unstretched rubber; (2) frozen rubber; (3) stretched rubber, 500 per cent elongation; (4) racked rubber, 2000 per cent elongation; film-specimen distance 3.4 cm.; (5) pale crepe rubber, 350 per cent elongation; room temperature; (6) pale crepe rubber, 350 per cent elongation; frozen.



FIGS. 7-12.—(7) pale crepe rubber, 250 per cent elongation; room temperature; (8) pale crepe rubber, 250 per cent elongation; frozen; (9) pale crepe rubber, 30 per cent elongation; frozen; (10) milled, compounded rubber, 200 per cent elongation; frozen; (11) vulcanized rubber. Cure: 40 minutes at 260° F., 200 per cent elongation; frozen; (12) vulcanized rubber. Cure: 240 minutes at 260° F., 200 per cent elongation; frozen.

of 250 per cent. The orientation after freezing is less perfect than at the higher elongation, as shown by the greater length of the spots. Figure 9 is the diagram from a piece of this same rubber stretched to 30 per cent elongation and frozen. At room temperature, no diffraction spots were discernible at elongations below 100 per cent. In Figure 9, the Debye-Scherrer rings have strong localized maxima, indicating a transition stage between oriented and random crystallization.

X-Ray effects due to the combination of stretching and freezing can also be observed with some vulcanized rubber stocks, although the general result of vulcanization is to inhibit or prevent the appearance of the phenomena altogether. Positive results were secured with the following compound:

	Parts by Weight
Pale crepe rubber	100
Zinc oxide	2
Sulfur	1.5
Mercaptobenzothiazole	.5
Stearic acid	.5

Figure 10 shows the diagram for the uncured, milled compound frozen with 200 per cent elongation. Strong fibering is evident. This uncured stock, due to the milling necessary for mixing, gave no indication of a fiber diagram at this elongation at room temperature. In fact, the diffraction spots were extremely weak at the highest elongation attainable. Figure 10 shows that there is sufficient structure left in the milled compound to get, by stretching, effective nuclei for an oriented crystallization at lower temperatures. It is also a fact that extreme breakdown due to heat and milling does not prevent the appearance of the Debye-Scherrer rings due to freezing.

Figures 11 and 12 illustrate that a forty-minute cure of this compound at 260° F does not prevent the appearance of a fiber diagram due to stretching and freezing, whereas a longer cure, 240 minutes at 260° F, causes the pattern to become very weak. The minimum elongation for diffraction spots at room temperature was 300 per cent.

Under proper conditions of stretching, which will be discussed in the next section, it is possible to freeze rubber with "higher orientation." Figure 13 is such a diagram for a frozen specimen, which, at room temperature, at this elongation, gave only a feeble diffraction pattern.

Fifteen or twenty exposures were taken with 0.039-inch gauge evaporated latex sheets to study changes during freezing in the patterns of samples stretched to 200 per cent and 300 per cent elongation, with and without higher orientation. The patterns did not seem of sufficient interest to measure or reproduce here, but the following qualitative observations are worthy of note. The alignment in the direction of the fiber axis is less perfect as freezing progresses. Especially in the case of higher orientation, the spots become somewhat longer. The reverse case, stretching rubber at a lower temperature, is known to give longer spots[5]. The extent of the higher orientation, as judged by the relative density of the equatorial spots, does not appear to change much during freezing. The x-ray pattern approximates its full intensity in a much shorter time than is required for the secondary elongation to approach its limiting value.

Occurrence of Higher Orientation in Stretched Rubber

Higher orientation in stretched rubber was first observed by Mark and von Susich[8], who obtained information necessary for the deduction of the unit

cell. In their work the phenomenon was shown for a thin stretched film, and the impression persists in the literature that thin films are necessary to show the effect. Sauter[9], however, secured higher orientation in racked rubber with

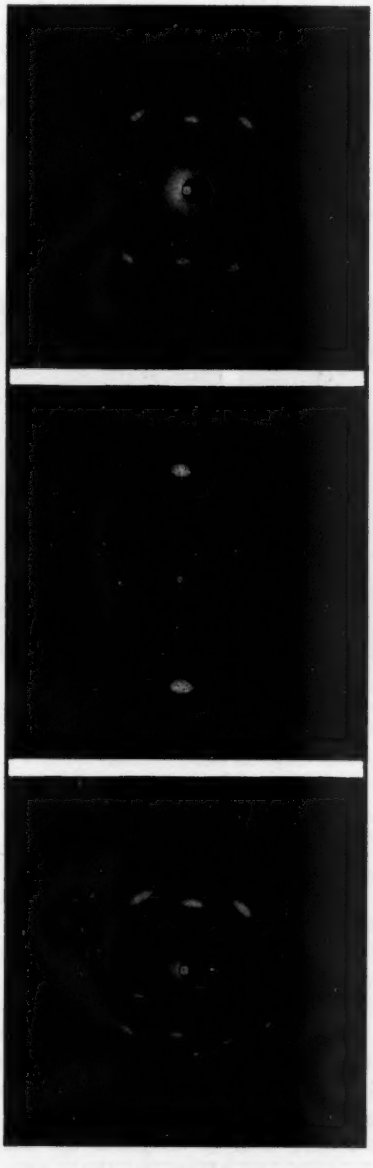


FIG. 13.—Evaporated latex. Elongation: 300 per cent, frozen. Sample 3 in. wide; 1 in. long.

FIG. 14.—Evaporated latex. Elongation: 900 per cent, room temperature. Length: 1 inch; width: 3 inches; gauge: 0.039 inch. Beam parallel to surface.

FIG. 15.—Evaporated latex. Elongation: 900 per cent, room temperature. Length: 1 inch; width: 3 inches; gauge: 0.039 inch. Beam perpendicular to surface.

a final thickness of one millimeter. There appeared to be an opportunity, by a quantitative study of the conditions of stretching necessary for the effect, to secure information in regard to the nature, perhaps the shape, of the crystallites or ordered regions responsible for the diffraction. The results follow.

Figures 14 and 15 are typical diagrams secured from stretched rubber showing higher orientation. For Figure 14, the path of the beam was essentially parallel to the plane of the stretched sheet; for Figure 15, the beam was perpendicular to this plane. By comparison of Figures 15 and 3, it is apparent that the relative intensity of the two innermost equatorial spots of the diagram affords a measure of the extent of the higher orientation. In the conventional notation, the first equatorial spot from the center is designated as A_1 and the second spot as A_2. An extensive series of measurements was made of the relative photographic densities of these spots under different conditions of stretching, the direction of the beam always being perpendicular to the plane of the stretched sheet. Figures 15, 16 and 17 were selected for reproduction to illustrate the changes in the relative intensities of A_1 and A_2 due to a systematic change in one variable in the stretching process, in this case, the distance between grips.

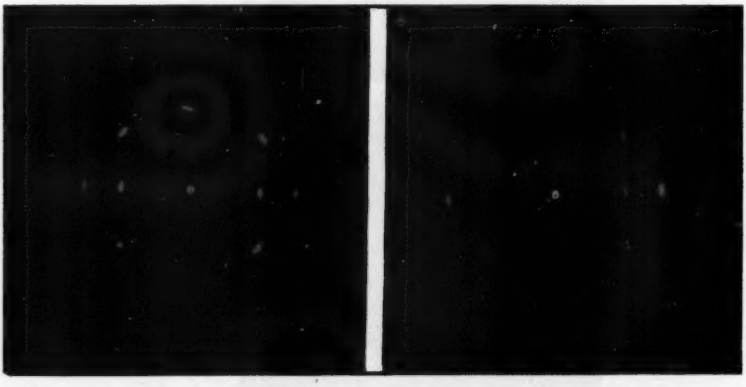


FIG. 16.—Evaporated latex. Elongation: 900 per cent, room temperature. Length: 2 inches; width: 3 inches; gauge: 0.039 inch.

FIG. 17.—Evaporated latex. Elongation: 900 per cent, room temperature. Length: 3 inches; width: 3 inches; gauge: 0.039 inch.

The rubber sheets for all this work were made by spreading appropriate thicknesses of ammonia-preserved latex on glass plates and drying at room temperature.

The higher orientation was found to depend on the geometrical variables in the stretching process, *i.e.*, the width, length and other dimensional changes of the test-piece due to stretching. Data illustrating this is plotted in Figures 18, 19, 20 and 21. Instead of plotting directly the photographic density ratio of the A_1 and A_2 spots, the ratio has been used to calculate the percentage of the diffracting crystallites which have their c axis essentially parallel to the width of the sheet. This has the advantage of making the data more readily comprehensible but the disadvantage of linking it with the structure of the unit cell, which cannot be regarded as finally determined[9-10]. It is always possible to calculate back to the photographic density ratio from the plotted values. There is no unanimity as to the letters used to designate the axes of the unit cell beyond the use of b for the fiber axis. Here, by the c axis is meant the axis with the dimension 12.6A.

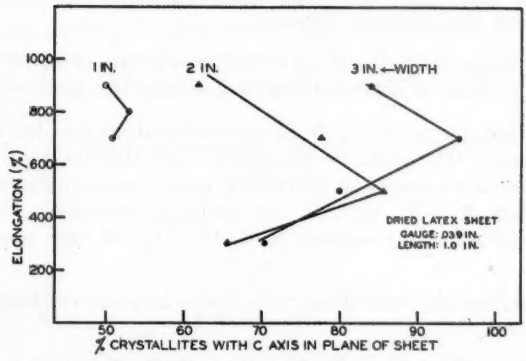


FIG. 18.—Dependence of higher orientation on elongation.

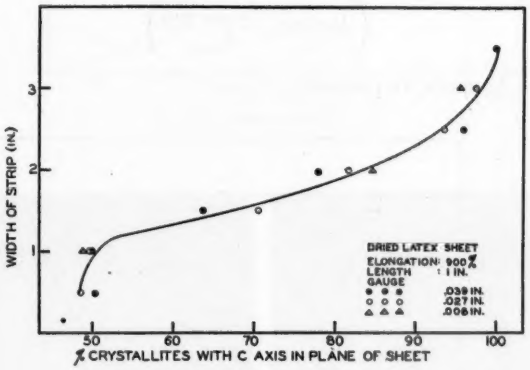


FIG. 19.—Effect of width on higher orientation.

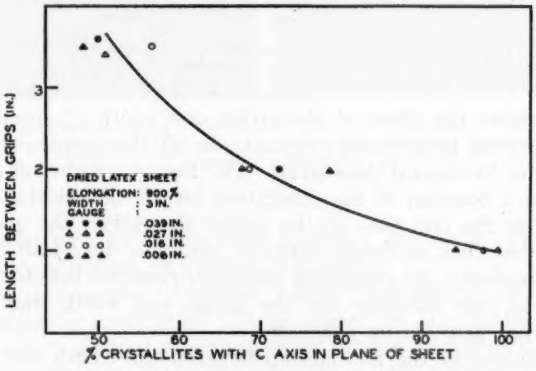


FIG. 20.—Effect of length on higher orientation.

Calculation of the percentage of the diffracting crystallites with c axis in the plane of the sheet was made as follows:

Let N_c = number of crystallites with c axis in the plane of the sheet.
N_a = number of crystallites with a axis in the plane of the sheet.

It is assumed that the ratio N_a/N_c is proportional to the density ratio of the A_2 to the A_1 spots. It should be recognized that this assumption is true only if the crystallites have the same diffracting power under different conditions of stretching. When $N_a=N_c$, that is, for ordinary stretching, the ratio of the density of A_1 to A_2 was measured as 0.618. Use of this constant gives the formula:

Percentage of diffracting crystallites with c axis in plane of sheet=

$$\frac{100N_c}{N_a+N_c}=\frac{100}{N_a/N_c+1}=\frac{100}{0.618D_2/D_1+1}$$

where D_2 and D_1 are the measured photographic densities

$$\left(D=\log_{10}\frac{I_{\text{background}}}{I_{\text{spot}}}\right)$$

for the A_2 and A_1 spots, respectively.

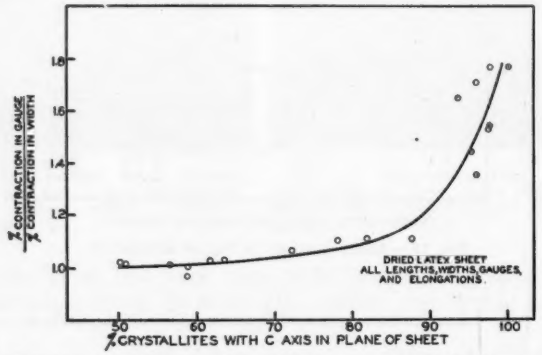


FIG. 21.—Relation of higher orientation to dimensional changes during stretching.

Figure 18 shows the effect of elongation and width of specimen, the gauge and length between grips being constant. In all the graphs, the gauge, width and length refer to original dimensions. The higher orientation reaches a maximum value as a function of the elongation for all the widths tried. This can be attributed to the fact that at the higher elongations the grips have moved so far apart that they no longer serve to maintain the width of the stretched rubber. Consequently, the stretching process approaches that for a narrow piece.

In Figure 19, the variables are the gauge and width, the elongation and distance between grips being constant.

Figure 20 illustrates the relationship between the length and higher orientation for all gauges tried, the elongation and width being constant.

In Figure 21 is plotted data for all gauges, widths, lengths between grips and elongations shown in the previous graphs. By using as ordinate the ratio

of the strain in gauge to the strain in width, the points fall on a smooth curve, which rises rapidly for extreme values of higher orientation. Thus, however it is achieved, an increase in this ratio from unity seems to be the essential feature of a stretching process which gives rise to higher orientation. It was shown to be possible in some cases to improve the higher orientation by stretch-

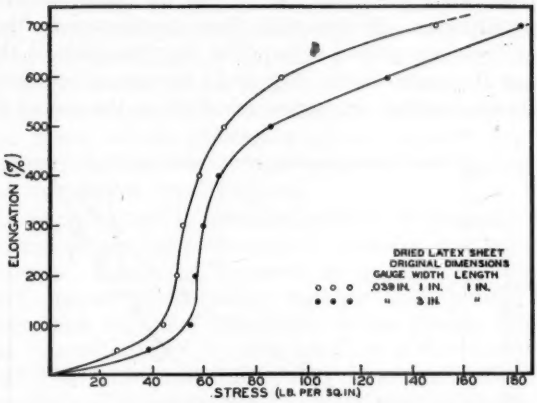


FIG. 22.—Stress-strain curves.

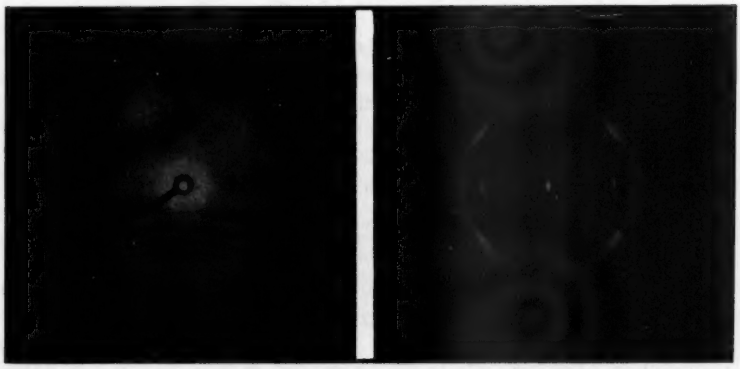


FIG. 23.—Evaporated latex. Elongation: 800 per cent, room temperature. Length: 1 inch; width: 1 inch; gauge: 0.039 inch.

FIG. 24.—Evaporated latex. Elongation: 800 per cent, room temperature. Length: 1 inch; width: 2 inches; gauge: 0.039 inch.

ing a sample sidewise after it had been stretched lengthwise. If this is carried too far it results, of course, in random orientation.

Greater stress is required to stretch rubber with higher orientation than is required for ordinary stretching. This is shown by the curves of Figure 22. This larger stress is associated with a more intense x-ray crystalline diagram. Figures 23 and 24 illustrate this. They are comparable x-ray diffraction patterns at rather low elongations for ordinary stretching and for stretching with higher

orientation, respectively. From the patterns, it is apparent that in the case of higher orientation the spots are stronger and probably would first appear at a lower elongation than is required in the case of ordinary stretching. The effect of maintaining the width during stretching may be considered as analogous to two-way stretching, which in turn is equivalent to compression perpendicular to the plane of the sheet. The effect of pressure is to raise the fusion point of rubber[11]. Hence the conditions of stretching for higher orientation are such as to favor crystallization. In line with these considerations there is an edge effect which results in less perfect orientation near the edge of the sheet.

Figure 25 gives the same plot as Figure 21 for several vulcanized pure gum stocks with different physical properties achieved by the use of different curing

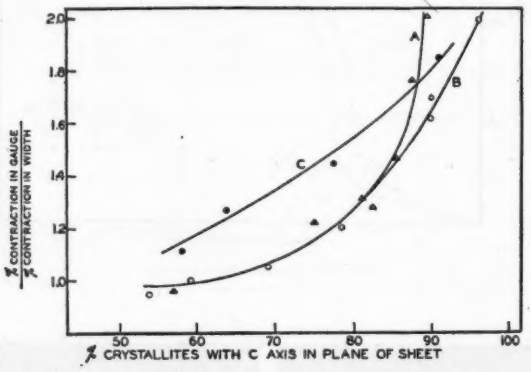


FIG. 25.—Higher orientation for vulcanized rubber stocks.

accelerators. The extent of the difference in physical properties can be seen from the data of Table I.

TABLE I

Compound	Tensile Strength Lb./Sq. In.	Stress (500% Elongation) Lb./Sq. In.	Final Elongation %
A	1990	342	800
B	2110	427	730
C	3270	995	675

It is very difficult to discern any variation in the x-ray diffraction patterns for stocks as similar as *A* and *B*. The curves shown represent one means by which the different internal structures may be made apparent in the x-ray diffraction phenomena.

DISCUSSION OF RESULTS

The results of the stretching and freezing experiments can be discussed in the same terms as the crystallization of a supercooled liquid. The amorphous diagram, as a starting point, may be taken as evidence of a characteristic liquid structure for unstretched rubber. The molecular groups of the ordinary liquid are simulated by small portions of adjacent long chain molecules. The differences from an ordinary liquid are to be largely accounted for by the idea that a single

long chain molecule can extend, probably in zigzag fashion, through a large number of such groups or relatively ordered regions. These conceptions are, in a general way, in harmony with recent theories of micellar structure[4].

Following the ideas of Tammann, the crystallization of a supercooled liquid proceeds from nuclear centers of crystallization formed in the liquid. These centers in rubber may be thought of as the ordered regions just discussed which undergo an improvement in internal molecular arrangement due either to a lowering of the temperature or to stretching. The rate of formation of nuclei and the velocity of crystallization depend on a number of factors, important among which is the mobility of the molecules. The fact that rubber chilled suddenly to liquid-air temperature remains amorphous can thus be explained by the general theory of the production of the vitreous state[12]. The rate of temperature change, in this case, is large compared to the rate of formation of nuclei and the velocity of crystallization.

The size of the crystallites in stretched rubber, as determined from measurements of the size of the diffraction spots[2] remains practically unchanged as stretching proceeds. Hence the increased intensity of the spots is attributed to an increased number of diffracting regions. An improved lattice structure at higher elongations may also contribute to the greater intensity. The size of the crystals reached when a liquid crystallizes is determined by the relative rate of formation of nuclei and the velocity of crystallization. In the case of rubber, the number of nuclei set up by the stretching depends, among other things, on the amount of the stretch. The growth from these centers is limited, probably in a statistical way, by the low mobility of the molecules, that is, an equilibrium condition is reached between the movement of portions of the long chain molecules into the lattice and thermal agitation.

It remains to consider the combined effect of stretching and freezing. These experiments show that stretching gives rise to incipient nuclei of crystallization partially aligned with the axis of stretching, an idea not entirely new[13]. Crystal growth from these centers may depend on the degree of perfection reached in the nuclei. Only at higher elongations at room temperature are the centers sufficiently perfect and definite to result in a crystal growth which becomes apparent by x-ray diffraction. When the temperature is lowered, centers, which may consist merely of an approximate parallelism of neighboring portions of a few long chain molecules, become effective for crystal growth. The velocity of crystallization from these centers is large compared to the rate of formation of new random centers due to the lower temperature. The result is a strong fiber diagram.

In the case of raw rubber, the perfection of the alignment of the nuclei along the axis of stretch and the number of nuclei is apparently inadequate to produce an appreciable fibering effect in the amorphous halo at room temperature before the diffraction spots appear. For vulcanized rubber such an effect has been reported[14].

The fact that stretched rubber can be frozen with higher orientation can be taken as an indication that the incipient centers of crystallization due to stretching possess in a rudimentary way all the symmetry characteristics of the crystal lattice.

The freezing of stretched raw rubber to give an oriented diagram is closely related to the phenomena of spontaneous molecular rearrangement observed for rubber by Thiessen and Wittstadt[15]. By means of optical refraction and x-ray diffraction, they showed that orientation phenomena continued for a

considerable period of time after the stretching. A definite equilibrium of the crystallized and amorphous components was reached, depending on the temperature and other variables. Spontaneous volume changes after stretching have been observed for vulcanized rubber by Holt and McPherson[16].

The work of Thiessen and Wittstadt has led them to regard rubber as consisting of a polyphase system in which, within a wide range of temperatures, crystals and fused substances of varying compositions are in an equilibrium which depends on the pressure. This concept of the crystallization process appears to be irreconcilable with a structure consisting of crystallites which are composed of mutually oriented portions of long chain molecules.

The most significant result from the study of the geometrical factors affecting the occurrence of higher orientation, from the standpoint of the internal structure of rubber, seems to be the quantitative connection between the extent of the higher orientation and the changes in lateral dimensions. Higher orientation results when the contraction in width of the stretched specimen is less than the contraction in gauge. This observation may have some connection with the shape of the unit cell[9-10], the long dimension of which, in the case of higher orientation, lies in the direction of the width of the stretched rubber.

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HIGHLY POLYMERIC COMPOUNDS.[1]

CLXIV. UNIT CELL DIAGRAMS AND THE MICROSTRUCTURE OF "SINGLE CRYSTALS" OF RUBBER

DETERMINATION OF THE LATTICE OF MACROMOLECULES OF RUBBER ACCORDING TO NEW X-RAY METHODS *

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DETERMINATION OF THE LATTICE OF RUBBER AS AN ANALOGOUS CASE TO THAT OF NATURAL CELLULOSE

After the discovery of a crystalline component in stretched rubber by Katz[6], determinations of the lattice from the fiber diagram were made by Hauser and Mark[7] and by Mark and von Susich[8]. These last investigators were able to obtain, for the first time, convincing facts regarding the lattice of rubber, and were able to produce and to study "ordered micellar structures" by stretching thin films of rubber to 1000 per cent elongation. By irradiating their specimens perpendicular and parallel to the plane of the films, they obtained fiber diagrams with characteristic differences in the intensity of certain interferences, which indicated a structure of the character of a single crystal in the rubber films. This was confirmed by a Weissenberg diagram of the fiber axis zone, from which it followed that the first two intense equatorial reflections A_1 and A_2 are located in the reciprocal lattice at an angle of approximately 90° to one another. As for the other equatorial reflections A_3 and A_4, it was assumed that they are the double orders A_1 and A_2, a fact which is not evident from the Weissenberg diagram. This results in a rhombic unit cell with a fiber axis period of 8.1 ± 0.1 A.U. and other periods of 8.3 and 12.3 A.U. However, based on the measured density of 0.955 for stretched rubber, the number of base molecules in the unit cell is 7.1. This should probably have been 8, and the great discrepancy indicated that there was still an error in the determination of the lattice.

The results were summarized in a model[9] of a unit cell of rubber, which is reproduced in Figure 1.

Mark and Meyer considered their results as proof that the four primary valence chains which pass through the unit cell are composed of isoprene residues, having, contrary to a concept advanced by Staudinger[10], a *cis*-configuration and arranged in the primary valence chain to form a sort of digonal screw axis.

A recent attempt to explain the discrepancies of the lattice of Mark and von Susich was made by Meyer and Lotmar[11] in 1936, who considered that they had succeeded in increasing the precision of determining the lattice. In this case they relied on the graphic evaluation of the fiber diagram according to a method developed by the present author[12], but without making any careful investigation of the errors which possibly entered into the determination[13].

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For the new monclinic cell obtained by this method, the following constants were obtained:

b (Fiber axis)	8.20 ± 0.5 A.U.
c	12.65 A.U.
a	8.54 A.U.
β	83° 20′

The new cell and the "precision" of its determination rests on the graphic indexing of a single interference, *viz.*, the A_4 reflection, which has been said to be an interference (304). From this the monoclinic axial angle was established, and thus in turn the remaining reflections. From these results, the spatial

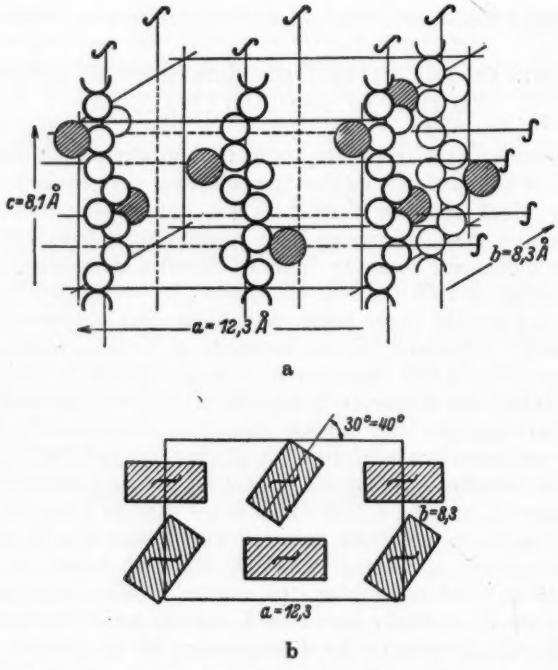

FIG. 1.—Unit Cell Diagrams of Crystalline Rubber and Digonal Primary Valence Axis Chains According to Mark, Meyer and von Susich (1928).

curve C^5_{2h} was deduced. A discussion of the symmetry relations between the four chains in the unit cell (according to C^5_{2h}) led the authors to the conclusion that stereometric right and left chains are unquestionably present in the cell, and that the crystal is to be regarded as a racemic molecule. Figure 2 will make this idea clear.

It follows from the foregoing discussion that the validity of the lattice of Meyer and Lotmar depends primarily on whether interference A_4 in the equatorial plane of the fiber axis zone is located at an angle about 45° to the direction of the A_1 (200) and A_3 (400) reflections, or at an angle of 90° (if A_4 is the second order of A_2 (002), *i.e.*, (004)). This question, which is typical of those encountered in determining lattices from fiber diagrams, would have to be finally decided with the aid of the new goniometric method for the unit cell

diagram, with a suitably prepared specimen of rubber. From this it would be possible to obtain an idea as to what extent it was justifiable to draw the conclusions above from the unit cell diagram of B-cellulose, described in the earlier work.

In what follows, it will be shown that the lattice of Meyer and Lotmar does not represent any step forward from that of Mark and von Susich and that it is based on erroneous measurements. The error of Mark and von Susich is pointed out, and the correct lattice and a new model of the unit cell are worked out.

PREPARATION OF THE SPECIMENS AND THE PHOTOGRAPHIC TECHNIQUE

The specimens of rubber, oriented in the characteristic form of a single crystal, were prepared in a way similar to that described by Mark and von

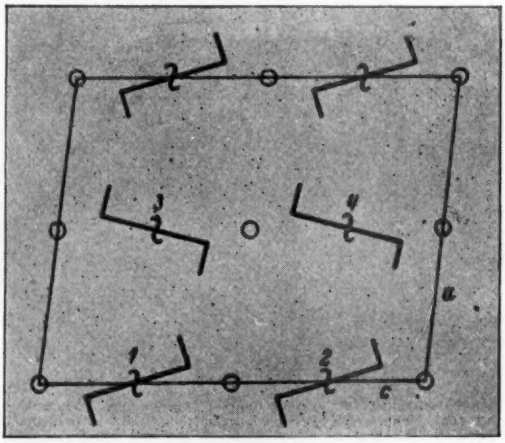

FIG. 2.—The new lattice of Meyer and Lotmar (1936), with supposedly established dextro- and levo-chains (racemate crystal).

Susich, *i.e.*, by stretching to a high degree (approximately 700 per cent) ribbons of *Hevea* crepe and smoked sheet rubber which had previously been "melted" by immersion in hot water. However, in the present study, the ribbons were stretched over a plate. They were of sufficient thickness so that rod-shaped specimens of approximately 1 sq. mm. cross-section and 1 to 5 mm. long could be cut from the rubber frozen by cooling with tap water.

If the fiber axis is designated as the *b*-axis, the direction perpendicular to this in the plane of the strip as the *a*-axis and that perpendicular to these two axes as the *c*-axis, then three kinds of test-specimens could be cut with a razor-blade from any strip. In two cases the 5-mm. edge was the *b*-axis and the *a*-axis, respectively; in the third case, one edge was the *c*-axis, *i.e.*, the specimens consisted of little cubes. In all cases the rod-shaped specimens were examined at temperatures between 0° and 25° C, under which conditions warming by contact with the hands had especially to be avoided, since this caused fusion and contraction to one-seventh of their length (by this means the exact elongation of a specimen could be estimated).

The specimens were then adjusted like single crystals in a cooled x-ray goniometric camera and in a vertical cone camera. The goniometric photographs were taken with a Seemann tube and a Müller tube, with copper radiation filtered through nickel; a Seemann monochromator for Cu-K_α radiation, with a specially chosen crystal of rock salt, was used for obtaining the spectral monochromatic cone fiber diagram. The time intervals for the photographs were 10-18 hours for the goniometric x-ray photographs and 40 hours for the monochromatic photographs, with a load on the tube, operated without rectification, of 30 kV maximum potential and 20 mA.

THE SPECTRAL MONOCHROMATIC FIBER ROTATION DIAGRAM

In the case of the rod-shaped specimens with the fiber axis on their long edge, spectral monochromatic rotating crystal photographs were first obtained, the aim being to obtain an idea of the character of all interferences under these conditions, and particularly to learn what equatorial and diatropic reflections

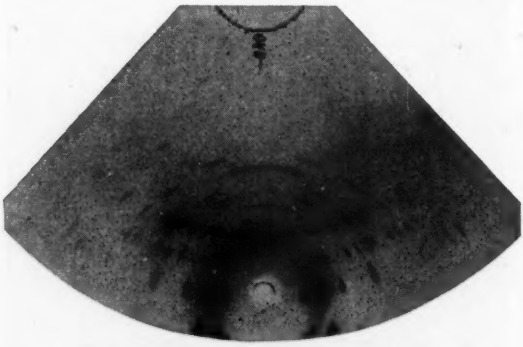

FIG. 3.—Spectral monochromatic rotation fiber diagram of a rubber rod, with a single crystal structure, elongated 700 per cent. The weak fiber base reflection (010) is present. No other weak interferences are present between the first four equatorial reflections. The excessive breadth of the two equatorial reflections should be noted.

might be present. In these diagrams the weaker interferences are especially clear, because the diagrams themselves are extraordinarily clear and full of contrast as a result of freedom from a continuous background and from β-radiation. The rotating crystal cone diagram is reproduced in Figure 3. From this diagram, complete measurements of which are omitted for the present, the following observations may be drawn:

(1) The very weak diatropic reflection (010) is plainly visible, and therefore extinction of the odd orders is not, strictly speaking, complete.

(2) No further reflections within the first four intense equatorial reflections are visible.

(3) In contrast to the crystal monochromatic fiber diagram of natural ramie, the line grating spectrum of the "ultracrystalline" fiber structure in the diagram of rubber is not visible on the equator or on the first layer line. However, a similar effect is indicated on the second layer line. Rubber crystallites are therefore thicker than cellulose crystallites by several orders of magnitude.

(4) The "double reflections" on the fourth and fifth layer lines which appear in the diatropic direction (perpendicular to the equator) on the cone fiber

diagram of natural cellulose are true reflections, which cannot originate from the radiation screen or from the focal point of the tube, for in the diagram of rubber this "effect" is not visible when the same photographic technique is employed.

THE EQUATORIAL UNIT CELL DIAGRAM OF SINGLE CRYSTALS OF RUBBER

The equatorial unit cell diagram of the fiber axis zone of the same specimen which was used to obtain the fiber diagram shown in Figure 3 was photographed with the rotating goniometric camera (constructed in the Seeman Laboratory at Freiburg i. Br.) and described in the earlier work. Here the rotating disc was in 45° position. This photograph is reproduced in Figure 4.

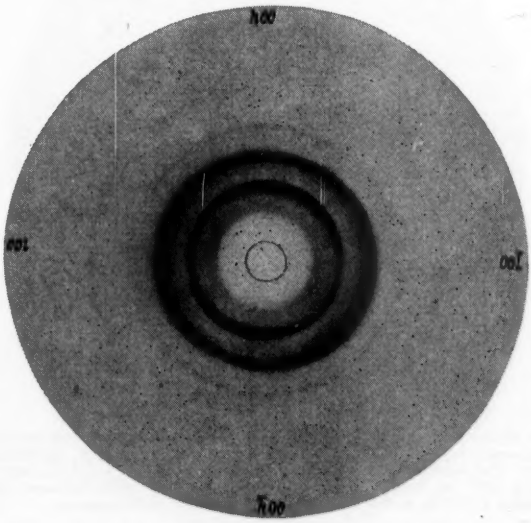

FIG. 4.—Unit cell diagram of the fiber axis zone (reflection (h0l)), which shows the 90° angle of the lattice planes for reflections A_1, A_2, A_3 and A_4. Contrary to the data of Meyer and Lotmar, the first order of A_4 is A_2.

(A_1=(200); A_3=(400); A_2=(002); A_4=(004)).

In Figure 4, one may imagine the S-shaped principal lines of the lattice drawn through the centre point of the diagram. The various orders of reflections of a definite lattice plane lie on one of these lines. Only two lattice lines are visible in Figure 4, and these are at an angle of 90° to one another. The intensity maxima A_1 and A_3 lie in the direction (h00)-($\bar{h}$00), and the intensity maxima A_2 and A_4 in the direction (001)-(00$\bar{1}$). If A_4 were an interference (403), as Meyer and Mark reported[14], the intensity maximum would have to lie at an angle of approximately 50° to the direction (h00)-($\bar{h}$00), and this would certainly be visible.

To check and confirm the statements regarding the unit cell diagram of the fiber axis zone, it is necessary to obtain the unit cell diagram of the other two chief zones, and therefore of the *a*-axis and *c*-axis. In the presence of a genuinely single-crystalline structure in the rod-shaped specimens of rubber used in the present investigation, only the reflections (00l), *i.e.*, A_2 and A_4, should appear

in the unit cell diagram of the *a*-axis zone (reflections 0kl) perpendicular to the lattice line (0k0)-(0$\bar{k}$0), provided that the *b*-axis is orthogonal. On the other hand it is to be expected that only the reflections (h00), *i.e.*, A_1 and A_3, are present in the unit cell diagram of the *c*-axis zone (reflections hk0) in a direction perpendicular to (0$\bar{k}$0)-(0k0). In this case the reflections (0k0) are the diatropes of the fiber base. The two photographs obtained under these conditions are shown in the diagrams of Figure 5 and Figure 6.

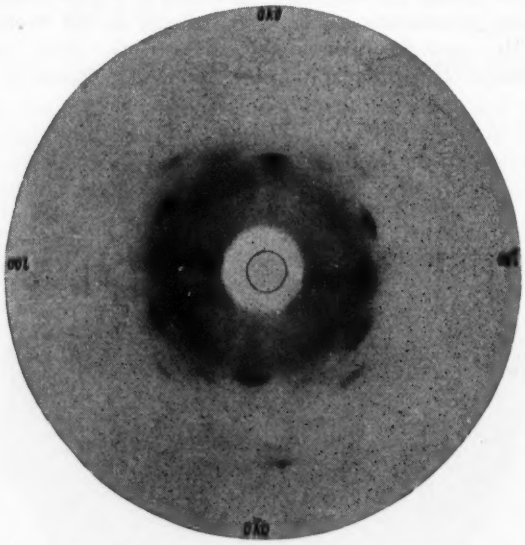

FIG. 5.—Diagram of the unit cell of the a-axis zone (reflection (0kL), because of imperfect orientation and incomplete single-crystal structure, several intense reflections, *e.g.*, interference A_1 (200) still come through feebly. The relation of A_4 to the lattice line of A_2 (002) and the halving of the translation in the direction (001) by reflection (021) are visible. The angle between (0k0) and (00L) is exactly 90°. The reflex (010) is invisible. The diagram is still underexposed.

TABLE I

GLANCING ANGLE OF THE EQUATORIAL REFLECTIONS OF THE FIBER DIAGRAM AND REDUCED VECTORS (TO $\lambda = 1$ A.U.) OF THE RECIPROCAL LATTICE

(Centre Measurements)

Reflection	Glancing angle	sin θ/λ=sin θ°	Index
A_1	7° 5′	0.0800	200
A_2	10° 30′	0.1182	002, 300
	Width 9° to 12°	0.101 to 0.135	
A_3	14° 10′	0.1587	400
A_4	20° 15′	0.2245	004
A_5	29° 30′	0.3195	800
A_6	35° 13′	0.3750	...
A_7	38° 0′	0.4000	...

With the aid of these diagrams it is easy to explain the shortcomings of the lattice of Mark and von Susich and the error in that of Meyer and Lotmar[15]. Table I gives first of all measurements of the equatorial reflections of the fiber diagram. In each case the centre of reflection was measured, but in the case of A_2 the width of the reflection is also recorded, since this is a double interference.

If reflections (300) and (002) are computed from the sin θ° values of reflections (200), (400) and (004), values of 0.1200 and 0.1123 are obtained. The width of the reflection A_2 is so great that the sin θ° values of the two boundaries extend above and below the calculated mean values, as may be seen in Table I (0.101 and 0.135).

Of the two reflections (002) and (300), reflection (002) is the more intense, as is evident in the unit cell diagram of the fiber axis zone, in which the intensity maximum of the A_2 ring is at (002). The dual nature of reflection A_2 explains why, in the diagram in question, the intensity maximum on the A_2 ring extends much farther than in the case of the other interferences, since the two reflections blend together in the ring. On the contrary, in the unit cell diagram of the

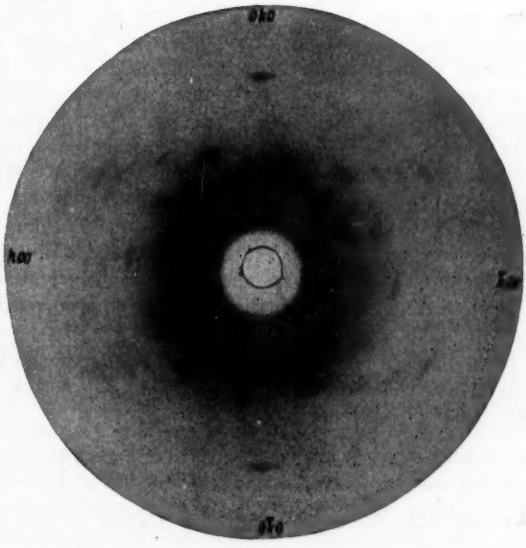

FIG. 6.—Unit cell diagram of the c-axis zone (reflection (hk0)). In this case reflection A_2 comes through much stronger in comparison with reflection A_1 than would be expected according to the preceding diagram, *i.e.*, it is quite obvious that reflection (300) is present along with (200)=A_2 and (400)=A_3 and therefore that A_2 is a double interference (=(002)+(300)).

a-axis zone and *c*-axis zone, (002) and (300) appear individually. In the fiber diagram, the adjacent interferences (002) and (300) overlap to form a single interference of great breadth. However, the sin θ° value, obtained from the centre measurement of this interference, does not seem to be related in any logical way to the sin θ° values of A_4 (004) or to that of A_1 (200)[16]. Mark and von Susich did not, in fact, identify the equatorial interference (300), whereas they indexed the other four interferences correctly. Nevertheless, in calculating the lattice constant of the *c*-axis, they used an incorrect centre value of A_2. On the other hand, as a result of accurate centre measurements of the A_2 and A_4 interferences, Meyer and Lotmar were forced to conclude that the data of Mark and von Susich had indexed them incorrectly. This in turn led them to the erroneous assumption that A_2 is interference (403) and that the lattice has a monoclinic axis. That it was possible to explain so easily this typical case of the derivation of a fiber diagram is proof of the special adaptability of the

modern x-ray goniometric method in studies of polycrystalline fibrous substances, *i.e.*, all types of fibrous and foliated structures. The determination of the lattice by Meyer and Lotmar is therefore incorrect to a much greater extent than ± 0.05 A.U.; the deviation for the *a*-axis is -0.37 A.U. from the correct value (8.91 A.U.). This order of magnitude is of interest because it shows that, even in relatively precise measurements of the diagram, values for the lattice may be indeterminate over a relatively great range if they are derived only from the fiber diagram.

THE NUMBER OF C_5H_8 RESIDUES IN THE CELL AND THE DENSITY OF STRETCHED RUBBER

The density of rubber stretched 700-1000 per cent is 0.960-0.965. Based on a density of 0.965, and on the lattice of Mark and von Susich, the calculated number of isoprene residues is 7.2. The difference between this value and the obviously correct value 8 exceeds greatly ordinary errors. Calculated from their new lattice (which is disproved in the present work), Meyer and Lotmar obtained a value of 7.6, which also is much too low, because the calculated roentgenographic density is 1.02 for a value of 8. The cause of the continuing discrepancies is ascribed to "a loose structure of the small crystallites." That this cannot be so is proved by a comparison of the crystal monochromatic fiber diagram of rubber with that of natural cellulose, in which the loose structure gives rise to a very intense line grating spectrum. Consequently the fact that there is no longer any lack of agreement between the measured and calculated densities must be regarded as further proof of the correctness of the new determination of the lattice.

On the basis of a rhombic lattice, the following values of the lattice constants for the *a*-axis and *b*-axis were obtained from the sin $\theta°$ vectors of (004), (002) and (200), (300), (400), (800) in Table I.

a ..... 8.91 ± 0.05 A.U.
c ..... 12.60 ± 0.05 A.U.

With a *b* value of 8.20, these values give a volume of the unit cell of 921 $(A.U.)^3$.

Based on a measured density of 0.965, the number of isoprene residues in the cell is 7.92. Conversely a roentgenographic density of 0.974 is obtained by calculation from the value 8. This density agrees far better with the experimental value than does the density of 1.02 mentioned above[17].

THE ARRANGEMENT OF THE MACROMOLECULES OF RUBBER IN THE LATTICE AND THE FORM AND SYMMETRY OF THE PRIMARY VALENCE CHAINS

Since the length of four chain carbon atoms in the isoprene residues cannot, by analogy with paraffin compounds, be greater than 4.8 A.U., whereas the fiber period of rubber is over 8.2 A.U., two of the eight unit molecules must lie one after another in the direction of the fiber axis, so that four chains pass through the cell. Meyer and Mark have taken the view that the two chain isoprene residues are united according to the manner of a digonal screw axis. They believe further that a *cis*-arrangement is present at the double bond of the isoprene residue, rather than a *trans*-arrangement, which they assign to gutta-percha and balata.

In earlier work, more general data on the arrangement of the repeating molecular groups as linear organic primary valence chains were offered[18], according to which digonal, trigonal, tetragonal and hexagonal screw structures are regarded as exceptional cases. In the cone fiber diagram of rubber the diatropic interference (010) is very distinct, although it is much less intense than (020), and (040). The extinction of the odd orders, which must be complete in the presence of a digonal screw axis, is therefore not exactly true in the present case, as in the case of natural cellulose.

If, however, the appreciable intensity of (010) is disregarded, and it is assumed that the law of extinction of odd orders is approximated fairly well, then there are various possibilities on which this can be based:

(1) The primary valence chains themselves have the symmetry of a digonal screw axis, as Meyer and Mark have assumed;

(2) Symmetry of a digonal screw axis actually exists among the various primary valence chains, which do not possess this symmetry themselves and are in fact unsymmetrical;

(3) There is, in the direction of the fiber axis, a halving of the translation in the sense that one primary valence chain is displaced by $\frac{1}{2}$ b with reference to the adjacent chain. This possibility merits consideration, since it may be the result of the principle of the close-packing of rod-shaped chains.

The digonal linking of the isoprene residues assumed by Mark and von Susich is, in contrast to that of glucose residues, without any constitutional chemical basis, although it has been suggested in connection with observations on the crystal structure of organic compounds of low molecular weights. However, the mutual linking, in the manner of primary valences, of the atoms of the repeating molecular groups of a predominantly homopolar linear macromolecular chain follows primarily the principle of the least disturbed valence activity, according to which in the crystalline state a field of force of the primary valence chains balanced to the greatest possible extent in the rod-shaped macromolecules takes part in the deformation of the valence forces through lattice forces; this leads to the establishment, with the least possible expenditure of energy, of a most probable, good periodicity of crystallization. This principle of intramolecular arrangement has in general nothing in common with the principle of intermolecular arrangement of macromolecules. These latter follow the rule of the structural theory of crystals and are, in the case of the crystallization of linear macromolecules, synonomous with the principle of the close-packing of rod-like chains.

From these points of view, a digonal rubber chain is really very improbable. If it were possible to explain the x-ray phenomena on the basis of an unsymmetrical primary valence chain by the arrangements (2) and (3) mentioned above, it would be all the more improbable. Other points are also to be considered. For example, the planar zig-zag chain, which is apparently well authenticated in the case of normal paraffins, is probably converted into the polymorphic columnar "tub" form by thermal disturbances or by disturbances by other kinds of atoms, *e.g.*, oxygen atoms and double-bonded carbon atoms; under these conditions this columnar form is the more stable one, for in this case the primary valence field of force can contract freely from its greatest length and thereby alter the symmetry, *e.g.*, bring about a transformation from rhombic to hexagonal or monoclinic symmetry. In general the longitudinal extension of the period of a primary valence chain represents, in a certain way, a state of equilibrium of the primary valence forces with the orienting inter-

molecular lattice forces. In the case of relatively hard hexagonal polyoxymethylene, the columnar chain is extended greatly (an average increase in length per chain atom of 0.96 A.U.); in the case of wax-like monoclinic polyethylene oxide the chain, although of the same form, is contracted to a much greater extent (average increase in length per chain atom of 0.72 A.U.). In the case of rubber with only chain carbon atoms, the average increase in length per atom is 1.025 A.U.; in the case of gutta-percha[19], 1.192 A.U.; in the case of normal paraffins, 1.25 A.U.

In the problem of the form of the polyisoprene chain, the question of *cis-trans*-isomerism at the double bond of the isoprene residue also plays a part. Mark and von Susich pictured the *trans*-form as a zig-zag chain similar to paraffin chains and, on account of the extended form, they necessarily assigned it to gutta-percha, so that the *cis*-form remained for rubber. To Mark and Meyer, this seemed to make it still more probable that the irregular form of the digonal helical chain must be regarded as the cause of the shorter length per isoprene residue. Recently Meyer and Lotmar, basing their view on the fact that "the form of chain adopted by Mark and von Susich can no longer be reconciled with present data," ascribed to the digonal rubber chain a spatial, *i.e.*, a columnar form, for which at least the valence angles can be determined.

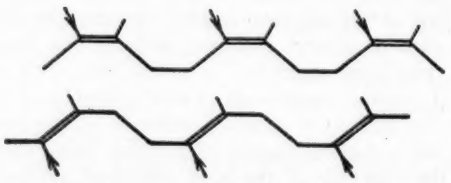

FIG. 7.—Two-dimensional projected cis- and trans-chains (diagrammatic). The contracted columnar form is attributable to a certain amount of free rotation around the C-C bonds with retention of the valence angle.

None of the forms of chain described above has been confirmed in a satisfactory way roentgenographically. One is therefore still confronted with the question whether other forms of chain may satisfy the principles already discussed regarding the crystallization of linear macromolecules. If one considers the double-bonded carbon atoms, with their somewhat smaller diameter compared with that of single-bonded carbon atoms, as a disturbing factor in the formation of normal zig-zag paraffin chains—an assumption which it is probably not possible to prove—then the formation of columnar shell-like chains appears to be favored, as is the case with polyoxymethylene. In the stretched condition, the tub-like form might assume almost a planar form, and in the contracted state it might be transformed, with preservation of all valence angles by utilization of a certain amount of freedom of rotation, by the C-C bonds into the columnar form. In the projection and reduction of the shell-like chains on paper, the *cis*- and *trans*-chains appear as in Figure 7.

The question then arises which of the two tub-like forms is to be ascribed to rubber or to gutta-percha. Apparently there are steric reasons (lack of space for the lateral methyl groups in the "tub") why a stretched polyisoprene tub-like chain cannot exist. This is a further reason for assigning the *trans*-form to balata and gutta-percha and the *cis*-arrangement to rubber, as was done by Mark and his collaborators. The constitutional formula of the *trans*-chain of rubber given by Staudinger[20] is, from the point of view of a model, equivalent

to the *cis*-chain of Mark and von Susich, for it too involves the principle of a digonal screw axis. If however, a stretched tub-like chain is impossible because of spatial requirements, one is led, in conformity with one of the reasons given by Staudinger (balata and gutta-percha have a regular molecular structure, rubber an irregular structure) to ascribe the *cis*-form to rubber.

Possibilities (2) and (3) described above are sufficient to explain the fundamental differences in intensity of the interferences on the three axial directions of the reciprocal lattice; in this case the principle of the closest packing of the rod-shaped chains must play an important part. In the direction of the a^+ axis of the reciprocal lattice, no special extinctions are to be observed, since (300) is very intense. Evidently there is extinction of the odd orders in the direction of the c^+ axis; and this is also approximately true of the b^+ axis. Of the various possible ways of explaining these intensity effects, the following arrangement deserves special consideration.

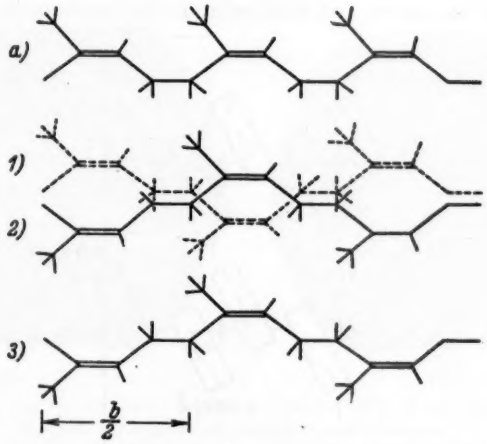

FIG. 8.—The type of packing of the columnar shell-like chains which probably exists in the lattice of rubber.

Evidently the *a*-surface is centered, so that in a first approximation a lateral, simple base-centered rhombic lattice is involved. The question then is in what way the four polyisoprene chains are oriented with respect to one another to form this face-centered lattice. This is possible in the following general way. Each two chains which are located in a general or independent position (on the *b*-axis) are oriented with respect to each other according to the symmetry of a digonal axis of rotation. One of the two digonal axes of rotation (not screw axes), which lie parallel to the fiber axis, occupy at the same time a lattice point, and the other axis of rotation is located on the *c*-axis at point *c*/2. However, in order that the *a*-face be centered, the last pair of chains must be displaced by *b*/2 along the fiber axis. The diagrams which follow (see Figure 8) illustrate first of all the two chains in digonal position to one another, and two other chains, where one is displaced by *b*/2 with respect to the other. Here *a* represents the tub-like chain projected in the plane of the paper, from which chain (1) is derived.

It is evident from the two diagrams that the principle of the closest packing of rod-shaped chains is adhered to particularly well. In the second case it is

evident that the displacement of two chains with respect to one another in the direction of the fiber axis can be explained by the fact that the lateral methyl groups of the isoprene residues have a tendency to pack more closely in the empty spaces of the adjacent molecules. Four closely packed macromolecules form as it were a flat unit lamella, which then forms the true molecular group; this occupies the lattice points of the face lattice perpendicular to the fiber axis, as shown in Figure 9.

Reverting now to the fact that extinction of the odd orders on the b^+ axis is not complete, a plausible explanation might be that to be described.

Exact centering of the *a*-face does not occur for two distinct reasons.

(1) With fewer than 2000 *trans*-isoprene residues, which are approximately the number in an undissociated macromolecule of rubber according to Staudinger and his collaborators[21], a certain number of repeating molecular groups with differing chemical structure may be present, *e.g.*, molecules with *trans*-isomerism at the double bond. The effect of disturbances of this kind could easily prevent the exact parallel alignment and positioning of the macromolecules.

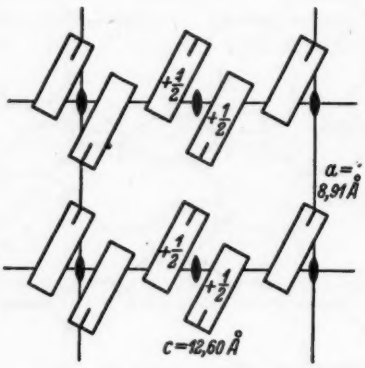

FIG. 9.—Projection of the chains on the base (b-surface).

(2) To attain close packing of the chains, whereby the lateral methyl groups tend to concentrate in the empty spaces of the chains, a displacement of the chains with respect to one another is necessary; this displacement does not amount to exactly $b/2$ but differs somewhat from this value. From this point of view, combination to an assembly of four units (elementary lamella) represents a primary association, which follows a secondary, somewhat less close packing of the lamellas. In the earlier work on the crystallization of cellulose chains, a similar view was expressed, and it is apparently of general significance.

The lamellar structure of the crystallites would therefore be particularly well defined in the submicroscopic dimensions. In view of the constant disturbances in the lattices of the macromolecules (aside from the fact that such large molecules cannot form as perfect a lattice as can small molecules), it is probably impossible to prove roentgenographically that oppositely directed primary valence chains, *i.e.*, racemic primary valence chains, are present in a lattice. Finally statements concerning spatial groups in the lattices of linear macromolecules can be made only with certain reservations, and probably the number of possible spatial groups should in general be reduced. However, in this connection it is impossible to say anything more definite until further investigations have been carried out.

THE MICROSTRUCTURE ("MICELLAR STRUCTURE") OF "SINGLE CRYSTALS" OF RUBBER

As roentgenographs showed, the strip of frozen rubber examined in the present work had a single-crystal structure for a length of about 10 cm. and a breadth and thickness of about 1-2 mm. It was therefore to be expected that microscopic examination of the specimen would give further information about this fine structure. Such information was of interest because, according to earlier investigations[22], ordinary crystallized rubber is supposed to have a "micellar structure" like that cellulose, *e.g.*, crystallites with a length greater than 600 A.U., a breadth of approximately 500 A.U. and a thickness of approximately 150 A.U. Such an order of magnitude could hardly be true in the present case, which concerns the spectral monochromatic fiber diagrams of rubber and cellulose. Accordingly it was to be expected that the crystallites of rubber would necessarily have microscopic or even larger dimensions, and that they

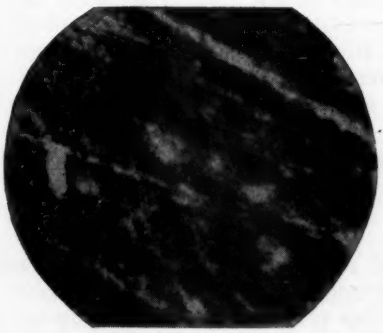

FIG. 10.

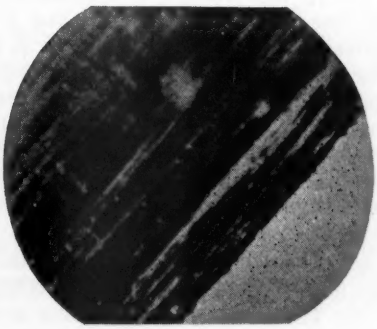

FIG. 11.

FIGS. 10 and 11.—Laminar microscopic crystallite region in stretched rubber.

FIG. 10.—Cross-section of a single-crystal specimen.
FIG. 11.—Longitudinal view on the edge of the specimen.
Magnification 186 times (Nicols).
Natural size.

would be imbedded in an amorphous material, which had not been affected by the stretching. Under the conditions described, stretched rubber crystallizes so readily that very large crystals can form from the nuclei. With the distribution of pressure and tension in the amorphous strip, as already described, and because of the peculiar properties, *e.g.*, tackiness, of the crystallites of rubber near the melting point (32° C), extensive crystallization throughout the mass is possible, and this must progress with accompanying orientation. Figures 10 and 11 show photomicrographs (magnification 186 times)[23] which were taken, in polarized light with crossed nicol prisms, of "single-crystals specimens," viewed both in cross-section and longitudinally.

It is evident from figures 10 and 11 that the non-crystalline phase is bright and that the doubly refracting phase is dark (negative reproduction). The photomicrograph of the cross-section is particularly surprising. It shows that a "single crystal" is composed of homogeneous crystalline lamellas in an extraordinarily regular manner, as in the case of a laminated artificial substance. The thickness of a single lamella is approximately 0.0015 mm. As for the breadth, the streaks extend almost across the complete field of vision. At a

lower magnification (50 times) a similar, although less pronounced, structure is still visible, and this lies in a direction almost perpendicular to the lamellar system described above. In the longitudinal photomicrograph it can be seen that the streaks do not lie exactly parallel to one another; rather they seem to penetrate one another in the manner of fibrils. Their length is naturally very great and can be distinguished only with difficulty.

With the aid of the photomicrographs and the roentgenographic investigation, it is possible to draw the following conclusions regarding the specific properties of rubber under tension.

(1) Even in the amorphous ("liquid") state there is extensive mutual orientation, *i.e.*, close-packing, of the macromolecules.

(2) During crystallization, partial separation takes place, whereby the non-extensible components (perhaps partially degraded or containing foreign impurities) form a loose, amorphous intermediate or cutaneous layer, in which the rather thick crystallites are enveloped.

(3) In the presence of surfaces of contact, which actually is nearly always the case, the rate of crystallization is very high in the direction parallel to the surface of contact and much lower in the direction perpendicular to this surface. The former is the direction of strong intermolecular cohesion, the latter is the opposite. Since in the "single-crystal" fine structure the contact plane lies parallel to the long side of the lattice, *i.e.*, the *c*-direction, the more dense arrangement of the macromolecules along this direction, which is shown in the model, is in accord with the observed facts. Whether the great power of orientation is in accord with an extensive planar form of the rubber molecule is difficult to say, but probably this is so.

(4) The laminar-fibrillar "tendons" of rubber may, as a result of similar and mutual orientation, grow together or interlock to a considerable extent.

(5) The effect of carbon black as a filler is characterized especially by the fact that the formation of relatively large crystalline regions is prevented, the system therefore becomes more highly dispersed from a fibrillar point of view, and this leads in turn to a considerable improvement in mechanical properties; at the same time the thermal effects are reduced. To a certain extent vulcanization has the same effect, since it hinders crystallization.

SUMMARY

1. The macromolecular lattice of rubber is rhombic and has the constants:

a	12.60 ± 0.05 A.U.
c	8.91 ± 0.05 A.U.
b	8.20 ± 0.05 A.U.

2. The number of isoprene residues in the cell is computed to be 7.92, *i.e.*, essentially 8; the density obtained roentgenographically is 0.974, which is in reasonable agreement with the value of 0.965 found experimentally. The discrepancies of earlier measurements are at the same time eliminated.

(3) The four chains which pass through the unit cell in the direction of the fiber axis are probably columnar tub-like chains with a *cis*-arrangement at the double bonds which are assembled after the manner of a lattice face-centered on one side.

(4) After being stretched to a considerable extent at ordinary temperature, eucolloidal "fused" rubber crystallizes with formation of microscopic crystalline regions of indefinitely great linear tension.

ACKNOWLEDGMENT

The author wishes to thank Professor Staudinger for his constant encouragement and support. The Scientific Society of Freiburg has been very liberal in providing further means for the completion of the x-ray equipment of the Freiburg Laboratory, for which we are especially grateful. Thanks are also due to H. Seemann for the various ways in which he aided in the work.

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[3] Meyer and Misch, *Helv. Chim. Acta* **20**, 232 (1937). In the note at the end of this work Meyer makes the following comments regarding the publication of the present author: "His conclusions, a part of which is purely hypothetical, are to a large degree the result of a faulty technique and of a misconception of the theory." In answer to this, one is referred to the work which follows.
[4] This is also true if this interference is the overlapping (016) interference of the first layer line, since by the goniometric method this shows its maximum intensity in the same location.
[5] Judged by new fibre diagrams on a 90° cone, (030) is also present.
[6] Katz, *Naturwissenschaften* **13**, 410 (1925).
[7] Hauser and Mark, *Kolloidchem. Beih.* **22**, 64 (1926).
[8] Mark and von Susich, *Kolloid-Z.* **46**, 11 (1928).
[9] Meyer and Mark, "Der Aufbau der Hochpolymeren Organischen Naturstoffe", Akademische Verlagsgesellschaft m. b. H., Leipzig, **1930**, p. 189.
[10] Staudinger, "Die Hochmolekularen Organischen Verbindungen: Kautschuk und Cellulose", Berlin, **1932**, p. 115; *Ber.* **63**, 927 (1930).
[11] Meyer and Lotmar, *Wien. Monatsch. Chem.* **69**, 115 (1936).
[12] Sauter, *Z. Kristallogr.* **84**, 453 (1933).
[13] Sauter, *Z. physik. Chem.* [B] **35**, 93 (1937).
[14] In this case the *a*-axis and *c*-axis are interchanged, with respect to the notation of Meyer and Lotmar.
[15] If the graphical indexing had been carried out as carefully for the remaining interferences of the fiber diagram, which actually was not done, the incorrect indexing of A_4 would have been noticed. In this case the extensive theoretical and hypothetical speculations of Meyer, which are concerned with this error, would have been obviated.
[16] According to these results, it is possible that the surprisingly broad equatorial interference of the fiber diagram of natural cellulose is also a double reflection. This subject will be taken up later.
[17] The suggestion of Meyer and Lotmar (*Wien. Monatsh. Chem.* **69**, 725 (1936)) that the anomaly in the density of the "inorganic rubber", polyphosphornitryl chloride, is even greater than in the case of rubber means, in view of what has been said, that the determination of the lattice of polyphosphornitryl chloride from its fiber diagram is subject to still greater errors.
[18] Sauter, *Z. physik. Chem.* [B] **21**, 179, 188 (1933).
[19] Fuller, *Ind. Eng. Chem.* **28**, 907 (1936).
[20] Staudinger, "Die Hochmolekulare Organische Verbindungen: Kautschuk und Cellulose", Berlin, **1932**, p. 115.
[21] Staudinger, "Die Hochmolekulare Organische Verbindungen: Kautschuk und Cellulose", Berlin, **1932**, p. 401.
[22] Meyer and Mark, "Der Aufbau der Hochpolymeren Organischen Naturstoffe", Leipzig **1930**, p. 196. See also von Buzagh, "Kolloidik", Dresden, **1936**, p. 137.
[23] These photomicrographs were prepared by (Frau) M. Staudinger, to whom the author wishes to express his gratitude.

THE CRYSTAL STRUCTURES OF CELLULOSE AND OF RUBBER *

H. MARK and KURT H. MEYER

PART I

Sauter[1] has made the statement that the interference A_2, which was reported by the present authors as a simple point, is the result of the superimposing of two interferences, which he designates as (002) and (300). In addition, he shows photographs of highly oriented rubber. In his diagram on page 725 of this issue of RUBBER CHEMISTRY AND TECHNOLOGY, it is evident that the strong reflection A_2 is quite distinguishable near the inner equatorial point A_1 ((200) according to Lotmar and Meyer[2]). However, as can easily be shown, Sauter has fallen into the same error that he did in his work on cellulose, *i.e.*, he has mistaken an incompletely oriented substance for a highly oriented substance. As far back as 1928 Mark and von Susich[3] published diagrams of highly oriented rubber[2], from which it was quite evident that in no case did the interference (300) show any notable intensity. This experiment was repeated by the present authors[4]. The illustration shows a diagram of highly oriented rubber and also a fiber diagram. The intensity of the interference (200), as well as that of (400), is approximately the same on the two diagrams. Whereas the reflection A_2 is very intense on the fiber diagram, only a slight intensity is visible in place of reflection A_2 on the photograph of the highly oriented rubber. Even if this intensity originated from the plane (300) it would obviously be much too small to bring about an appreciable displacement of the approximately twenty-times stronger reflection (002) on the fiber diagram. Sauter's displacement of the interference (002) in relation to the position assigned by Mark and von Susich, as well as by Lotmar and Meyer, is therefore without foundation experimentally and consequently his unit cell is invalid.

In addition to this, Sauter fails to discuss spatial groups in any way which might lend support to this point of view regarding symmetry, arrangement of chains, etc.

Consequently there is no good reason for going into detail about Sauter's hypotheses on chain form, rod-like chain packing, etc.; it may merely be pointed out that in this 163rd communication on high polymers, the *cis*-structure of rubber which was proposed and verified by Meyer and Mark[5] in 1928 was adopted, whereas Staudinger[6] has on the contrary always upheld the *trans*-structure.

The phenomenon described in such detail by Sauter, whereby larger crystal regions are formed when rubber is stretched, has already been observed and described by Hengstenberg[7].

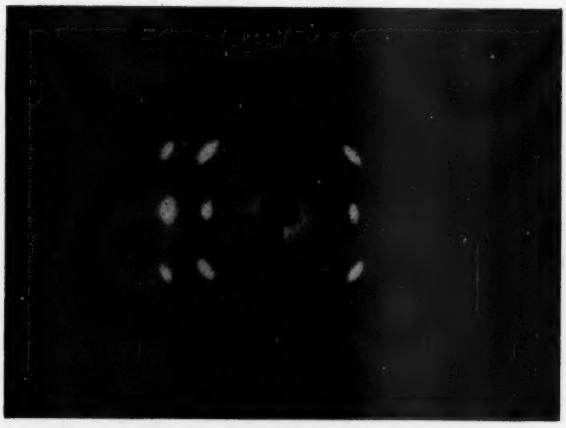
PART II

The second part of the paper is concerned with Sauter's work on the crystal structure of cellulose and is omitted here.

* Translated for *Rubber Chemistry and Technology* from the *Zeitschrift für Physikalische Chemie*, Abteilung B. Vol. 38, No. 6, pages 395-399, February 1938.

PART III

The treatment of fiber diagrams is so highly developed, both with respect to technique and to theory, that one should now expect certain general principles to be followed in the photographic process and in the methods of calculation. Since, however, in our opinion the investigations of Sauter unfortunately do



Left half: Fibre diagram of stretched rubber.
Right half: Diagram of highly oriented rubber, irradiated perpendicular to the plane of the film.

FIG. 1.—Copper Kα radiation; distance 40.5 mm.

not conform to these requirements[8], an extended discussion of the results of his work does not seem to be of much advantage. Nevertheless, we are ready and willing to continue the discussion on the structure of cellulose and of rubber whenever new and convincing facts are offered.

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[2] Lotmar and Meyer, *Ber. Akad. Wiss. Wien. math.-naturwiss.* [IIb] **145**, 721 (1936).
[3] Mark and von Susich, *Kolloid-Z.* **46**, 11 (1928).
[4] We are indebted to (Frl.) L. Misch for the roentgenographs.
[5] Meyer and Mark, *Ber.* **61**, 1939 (1928); "Aufbau der hochpolymeren Naturstoffe", Leipzig **1930**, p. 195.
[6] Staudinger, "Die hochmolekularen organischen Verbindungen", **1932**.
[7] Meyer and Mark, "Aufbau der hochpolymeren Naturstoffe", Leipzig, **1930**, p. 196.
[8] This is also true of the work by Sauter, which appeared recently in the *Z. physik. Chem.* **37**, 162 (1937), in which, among other things, faulty illustrations of an alleged focusing of the diatropes (see page 162), as well as the appearance of (0u0) (see page 163) are offered and greatly overexposed reflections (Figure 1) are used for making comparison of intensities (see page 166).

FORCED AND SPONTANEOUS CHANGES IN THE ARRANGEMENT OF THE MOLECULES IN STRETCHED RUBBER

CRYSTALS AND FUSED PHASE IN STRETCHED RUBBER [1] *

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INTRODUCTION

An unsaturated hydrocarbon of the formula $(C_5H_8)^2{}_x$ is the basis of natural rubber. Although there are still differences of opinion about the size of the molecules[3], it may nevertheless be accepted as fairly certain that the parent substance, the unsaturated hydrocarbon, is composed of a mixture of various steps of polymerization[4].

At ordinary temperatures and under no mechanical stress, both vulcanized and unvulcanized rubber are isotropic glasses. Exposed to x-rays they give the diagram of an amorphous substance, *i.e.*, a broad, diffuse ring. As a result of mechanical deformation, especially stretching, rubber becomes anisotropic. This anisotropy is manifest by the appearance of optical double refraction[5], as well as by an x-ray fiber diagram[6], which replaces the amorphous ring. This indicates orientation of the molecules and rearrangement into a space lattice, measurements of which have been made repeatedly[7] and which make probable a rhombic structure.

EXECUTION AND APPLICABILITY OF THE EXPERIMENTAL METHODS

It was found, during the course of the present investigation, that parallel examination by polarized light and by x-rays is of considerable aid in gaining an insight into the phenomena of this orientation and into the nature of elastic deformation. For measurements in polarized light and observations by x-rays supplement one another. In investigations by polarized light, it is a prerequisite that a fairly transparent rubber is available. The following comparison of the two methods will make clear their adaptability as well as their advantages and disadvantages.

The characteristics of the x-ray reflections make it possible to explain fairly clearly the changes which take place during stretching in the arrangement of the molecules. Furthermore they throw light on the mechanism of the process of orientation. They do not depend on the optical transparency of the material. However, the utility of this method begins only at a relatively high elongation. Furthermore roentgenographs unfortunately consume time, during which it is possible that progressive changes take place in the sample under examination. If this is so, a roentgenograph represents an integration of all the conditions through which the rubber passes while the roentgenograph is being taken. In addition to this, a quantitative determination of the anistropy, *i.e.*, of the

* Translated for *Rubber Chemistry and Technology* from the *Zeitschrift für Physikalische Chemie*, Abteilung B, Vol. 41, No. 1, pages 33-58, September 1938.

oriented phase, involves certain difficulties in that the diagrams must be measured photometrically under rigorously controlled experimental conditions and only then can be evaluated.

Some of these disadvantages are avoided by examination by polarized light. The mere fact that a slight elongated thread shows appreciable anisotropy, the sign and magnitude of which can be measured quickly by means of a Babinet compensator, is evidence in itself of the great sensitivity of this method. By means of such a quick method of measurement it becomes possible to detect sudden changes in anisotropy quickly and reliably. This ability to follow uninterruptedly all changes in anisotropy by measurements of changes in the double refraction makes it possible to obtain a continuous picture of the progress of orientation, whereas with the roentgenographic method it is possible to detect only comparatively few of the individual stages of orientation.

The necessity of using both methods at the same time is evident for the following reasons. The total double refraction as measured is made up of different constituent parts, including the forced double refraction and the characteristic or specific double refraction. The forced double refraction results from the mechanical deformation of the originally isotropic amorphous substances, and can be followed to the point where the lattice arrangement appears.

With the beginning of crystallization, the specific double refraction of the crystallites becomes superposed, whereby a part of the forced doubly refractive substance changes to a lattice arrangement. For this reason the increase in double refraction which is observed experimentally is the difference between the mean specific double refraction of the crystallites and the forced double refraction of the non-crystalline phase. Hence this increase depends on the proportion of the crystallized phase.

Although a complete separation of the forced double refraction and the specific double refraction is not possible, yet the combined use of the roentgenographic and optical polarization methods of investigation offers a fairly reliable experimental technique for the solution of fundamental problems.

Furthermore the combined use of the two methods makes it possible to recognize whether the oriented crystallites in the stretched rubber thread are twisted irregularly with respect to one another, and therefore whether their remaining degrees of freedom around the fiber axis represent a completely disordered state. It would in fact be expected that a triaxial index ellipsoid would be associated with a crystallite of rhombic structure and therefore that the double refraction would be biaxial. Consequently at a higher orientation of the crystallites a high double refraction is also observed, which depends on the direction in which the measurements of the anisotropy are made. Since it is doubtful whether a completely three-dimensional alignment of the crystallites is reached directly, it was considered of importance, as a simple working basis, to assume complete disorder of the crystallites around the fiber axis; in this case only a mean, although definite, specific double refraction is observed. In view of this, the cross-section of the specimen was so chosen that it did not depart too greatly from a square form and, in obtaining roentgenographs of the fibers, it was made certain that the direction of the reflections did not depend on irradiation perpendicular to the fiber axis.

A soft vulcanized rubber was used as matérial for the investigation[8], since unvulcanized rubber shows flow phenomena[9], which can be neither avoided nor disregarded, and the undesirable effects of which may vitiate the results. Nevertheless, as far as crystallization is concerned, the phenomena which are

observed with vulcanized rubber are true, in their essential features, of the same material before vulcanization. The nature of the elastic and anisotropic phenomena is the same for both unvulcanized and vulcanized rubber, although vulcanized rubber must be elongated to a greater extent for the fiber diagram to appear. The fiber diagrams themselves are, however, identical in the number, position and gradation of the intensities of the reflections[10]. This is proof that the structures of the crystals cannot differ essentially from one another. It follows also that the anisotropic phenomena conform to the same basic principles.

MEASUREMENTS OF THE OPTICAL ANISOTROPY

Figure 1 shows the way in which the double refraction[11] depends on the degree to which the rubber is elongated, under conditions where the rate of elongation is uniform. The temperature was 20° C. An appreciable optical anisotropy appears immediately after the beginning of elongation. With increase

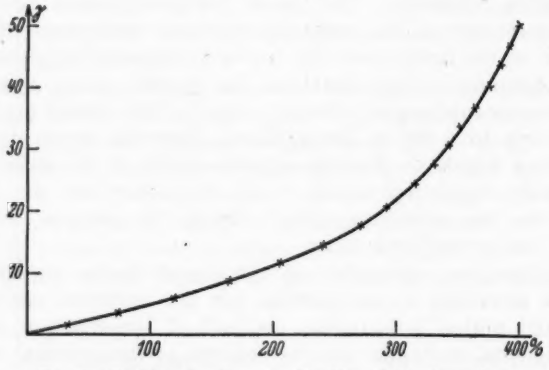

FIG. 1.—Double refraction as a function of the elongation.

Elongation to 400 per cent in 8.53 minutes.
Abscissa=Elongation as percentage of the original length.
Ordinate=Double refraction in sodium-light units, calculated on a basis of 1 mm. thickness.
Temperature 20° C.

in elongation the double refraction increases uniformly until the range of elongation has reached 250-300 per cent. Beyond this range the curve changes in direction, and simultaneously with this change in direction of the double refraction curve the first indications of a lattice arrangement appear in the x-ray diagram. Above this range the double refraction values and the increase in sharpness of the reflections run parallel with the degree of elongation[12]. At higher elongations the reflections of the lattice appear clear, and increase in intensity at the expense of the amorphous halo. From this point on, the double refraction increases at a much greater rate than at the beginning. Figure 2 is a reproduction of an x-ray diagram which was obtained from a rubber thread stretched to a high elongation.

These orientation phenomena are to a considerable extent reversible. In the case of natural rubber, the reversibility of these processes is obstructed by flow and retardation phenomena which, after prolonged mechanical stress, result in permanent deformation. In the case of vulcanized rubber these phenomena are insignificant within a wide range of temperature and can be disregarded[13].

The curve in Figure 1 does not show the true dependence of the double refraction on the degree of elongation; instead, it merely shows the relation between double refraction and elongation as influenced by a series of variables which depend on the method of measurement employed. However, it is possible to classify the phenomena, as will be seen in the following discussion.

SPONTANEOUS CHANGE IN THE MOLECULAR REARRANGEMENT

Judged by previous experiments, the process of molecular rearrangement apparently comes to an end when stretching is stopped or at least very shortly

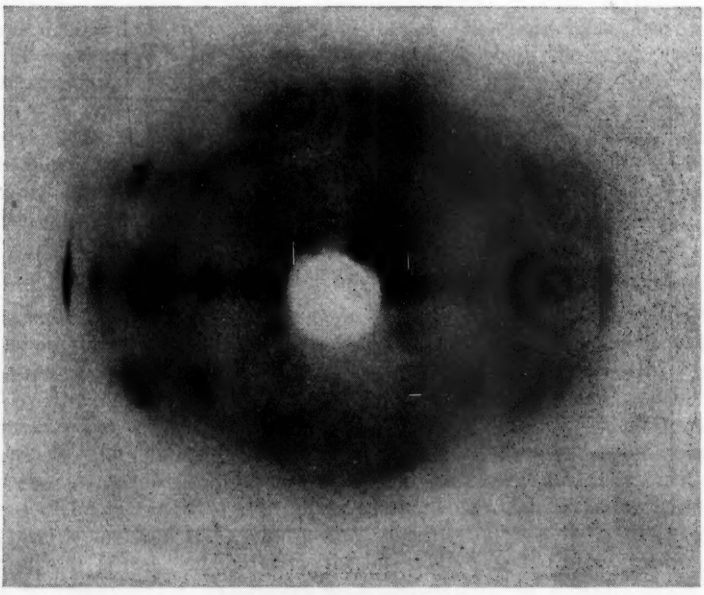

FIG. 2.—x-Ray diagram of a vulcanized rubber thread elongated to 550 per cent.
Taken with FeK-radiation.
Seemann x-ray chamber with zero sphalerite.
Diameter 114.4 mm.
Irradiation for 40 hours.
The inner equatorial interferences correspond to the conjectured but hitherto unidentified first orders, the position of which has been calculated by Mark and von Susich.

afterwards[14]. Accordingly it would be expected that the value of the double refraction which is obtained experimentally for a rubber band stretched rapidly would remain constant. Actually, however, above a definite elongation, the double refraction increases spontaneously[15]. This increase takes place at a high rate for several minutes, and then gradually dies away; however, it is still appreciable, in fact can be measured, even after several hours. The change in anisotropy after the rubber is stretched no farther (spontaneous rearrangement) was determined after the rubber had been elongated to various extents (preliminary stretching). Figure 3 shows the double refraction as a function of the time after the rubber had been stretched to various extents and then held at constant temperature.

In the experiments from which the data shown in Figure 3 were obtained, the specimens were clamped in a stretching device (see later), were brought to the desired temperature, were then stretched rapidly for about 3 seconds, and were fastened in position. The temperature of the chamber in which the specimens were stretched was maintained constant throughout the measurements.

It is evident that for each elongation the anisotropy reached a definite value immediately and, at elongations up to 285 per cent, the double refraction remained constant after the rubber was stretched no farther. Above this range of elongation, the spontaneous double refraction increased rapidly at first, then at a diminishing rate so that, after several hours, it reached a final constant value.

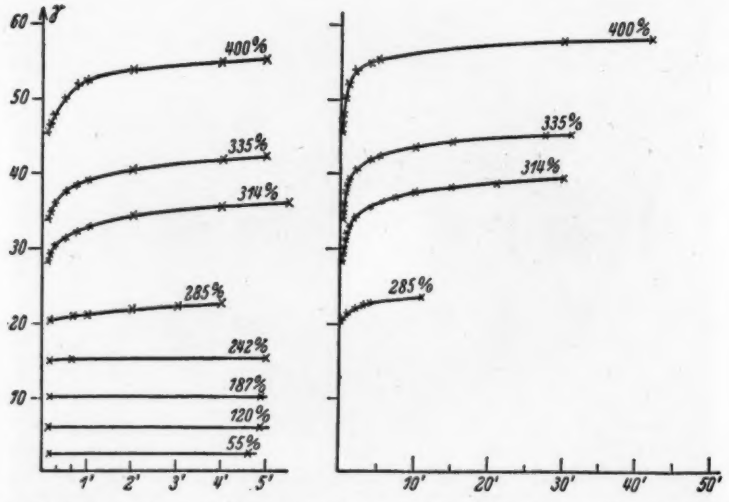

FIG. 3.—Spontaneous change in double refraction with time after rapid elongation. (Measured at various degrees of elongation.)

Abscissa=Time in minutes (two different scales).
Ordinate=Double refraction in Na-light units for 1 mm. thickness.
Parameter=Percentage elongation.
Temperature 20° C.

This spontaneous increase in the double refraction can be explained by a spontaneous post arrangement of the molecules. This phenomenon was manifest by the increasing clearness of the reflections in a series of x-ray diagrams which were obtained with the shortest possible times of exposure after the rubber was stretched no farther. These reflections increased in intensity at the cost of the diffuse ring (halo), without however changing their position.

This spontaneous arrangement in the lattice which took place gradually was most clearly observed by means of x-rays at an elongation slightly above that range at which the first indications of a progressive change in double refraction became evident. At this point the development of the sharp lattice reflections in the amorphous halo showed the maximum contrast.

At first thought, one might be tempted to attribute the spontaneous increase in the double refraction and in the lattice interferences to a retardation which depends on a slow temperature equilibrium between the temperature of the

chamber and the temperature of the rubber thread, which latter increases during stretching. The increase in temperature which took place during stretching is however too small to account for this; moreover, heat equilibrium between thin rubber specimens and the surrounding medium is reached in a very short time, as preliminary experiments have demonstrated.

The spontaneous increase in double refraction, according to the parallel experiments with x-rays, depends on a lattice arrangement of the molecules and corresponds to a crystallization whose appearance and progress depends in turn on the degree to which the rubber has already been elongated.

These phenomena can be explained on the assumption that crystallization takes place in the fused phase and that the progress of this crystallization is influenced considerably by pressure[16]. Although the stress is applied in only one direction, there is a certain pressure effect in each of the other directions, which is manifest in an increase in density during stretching. However, the effect of this stress is not directly comparable with the effect of pressure, since application of a stress causes an elongation whereby an alignment of the molecules takes place. One might regard this alignment as the active agent in bringing about crystallization with as much justification as to regard crystallization as a pressure effect.

INFLUENCE OF PRESSURE ON CRYSTALLIZATION

The influence of pressure on the crystallization of natural rubber was confirmed by an investigation of Thiessen and Kirsch[17]. It was found that the temperature of crystallization of unvulcanized rubber can be raised several degrees by the application of pressure in all directions, which prevents any prearrangement of the molecules. From this it is obvious that previous arrangement accelerates crystallization, although obviously it does not actually initiate the process. A definite minimum pressure is necessary for crystallization to commence. The quantity of crystalline component which is formed from the fused phase depends on the pressure and therefore on the previous stress, and an equilibrium is reached between the crystalline and fused phases. With increase in pressure this equilibrium is displaced toward a state where more crystallites are formed or where these crystallites increase in size. Also when the stress is diminished, the proportion of the crystalline component decreases and more amorphous fused phase is again formed.

INFLUENCE OF RATE OF ELONGATION ON THE MOLECULAR ARRANGEMENT

If an equilibrium has been reached, it is unimportant whether the particular state of mechanical strain is reached instantly or only gradually. The proportion of crystallized component and therefore the sharpness and intensity of the x-ray interferences compared to the amorphous halo was, in fact, found to be independent of the rate of elongation.

A series of vulcanized rubber threads was stretched to an elongation of 400 per cent at a strictly uniform rate at room temperature over a period of 60 days. At the time these experiments were begun, similar samples for comparison were stretched rapidly to the same elongation and maintained under the same conditions as those of the samples which were being stretched very slowly. After the slowly stretched threads had been elongated to 400 per cent, roentgenographs

of both series were taken. No difference in sharpness and intensity of the reflections of the two series was recognizable. The final molecular arrangement does not, therefore, depend on the rate at which rubber is elongated.

DEPENDENCE OF THE STATE OF ORIENTATION ON THE TEMPERATURE

It was to be expected that the state of equilibrium, which appears to depend so much on pressure, would be decisively influenced by the temperature of the rubber during elongation. It was logical, therefore, to investigate the spontaneous increase in ordered arrangement within various ranges of temperature. The experiments were carried out at 20°, 40° and 60° C, and the measurements were made in the same way as those already described. Whereas at low elongations the temperature had no appreciable influence, at higher degrees of elongation it had

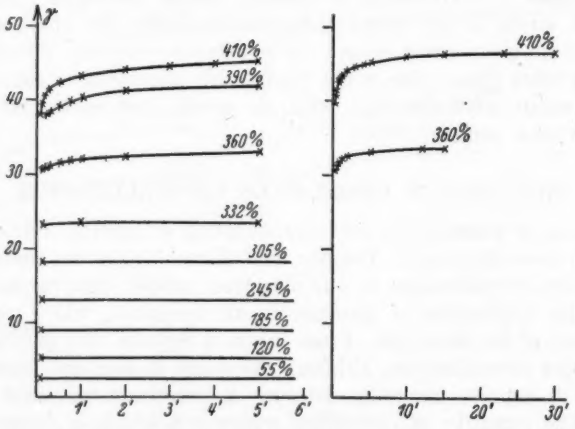

FIG. 4.—Spontaneous change in double refraction with time after rapid elongation. (Measured at various degrees of elongation.)

Abscissa=Time in minutes (two different scales).
Ordinate=Double refraction in Na-light units for 1 mm. thickness.
Parameter=Percentage elongation.
Temperature=40° C.

a very considerable influence. It was found that the higher the temperature the higher was the degree of elongation necessary to bring about spontaneous molecular arrangement. At the same time, the higher the temperature, the smaller was the increase in double refraction (see Figure 4).

The trends of the curves show that at higher temperatures the increase in double refraction at the beginning was relatively rapid, but also that it died away relatively rapidly. The final value toward which the double refraction approached was reached in relatively short times at the lower temperatures.

This fact means that the rate at which equilibrium was reached was increased by a rise in temperature. This phenomenon is explainable by the increased mobility of the molecules and the resulting lowering of the viscosity. In this way the molecules have the opportunity to arrange themselves, from an energy standpoint, in their proper positions in a shorter time.

Examination by x-rays confirmed the results of double refraction measurements. The higher the temperature, the greater was the degree of elongation necessary to develop a fiber diagram[18]. The lowest degree of elongation which was neces-

sary lay, in each case, within the range where a spontaneous increase in double refraction took place.

Figure 5 records graphically the individual measurements of the double refraction, at three different temperatures, as a function of the degree of elongation. The curves of the measurements made 1 minute and 5 minutes after the rubber was stretched no farther show the spontaneous molecular arrangement which took place. The anisotropy measured at low degrees of elongation was merely a forced double refraction, and under the experimental conditions it showed no appreciable dependence on temperature and did not increase after the rubber was stretched no farther. This might indicate that the average position of the molecules, which the experimentally measured double refraction indicated, was not changed by an increase in temperature at constant elongation.

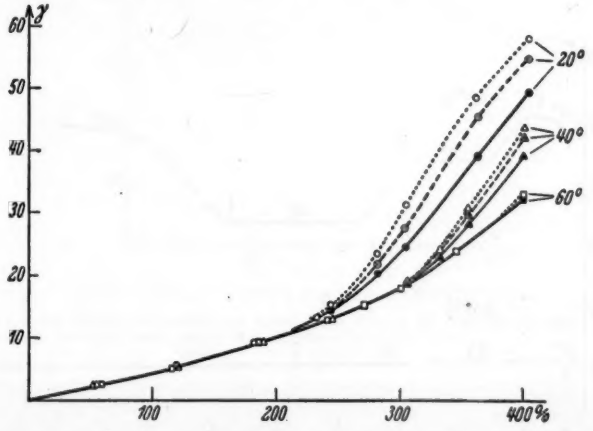

FIG. 5.—Double refraction as a function of the degree of elongation at temperatures of 20°, 40° and 60° C.

The curves were constructed from individual measurements during rapid elongation. The heavily drawn curves give the values 10 seconds after rapid elongation; the broken curves give the values 1 minute after elongation; the dotted curves give the values 5 minutes after elongation.
Abscissa=Percentage elongation.
Ordinate=Double refraction in Na-light units, based on 1 mm. thickness.
Parameters=Temperature and time after rapid elongation.

If the measured strain increases to a higher value, this can be attributed to an increase in mobility resulting from the higher temperature, in harmony with the views of Meyer, von Susich and Valkó[19], Meyer, Ferri and Hohenemser[20], Kuhn[21] and Mark and Guth[22]. On the contrary, the arrangement of the molecules is greatly influenced by the temperature within the ranges where spontaneous orientation can be observed.

To attain the same lattice-like arrangement at higher temperatures, the pressure must be higher, resulting in a higher elongation. The distance of the broken and dotted curves from the solid line in Figure 5 indicates the general order of magnitude of the rate at which spontaneous arrangement took place.

THE PROCESS OF FUSION IN STRETCHED CRYSTALLIZED RUBBER

In connection with these ideas, the attempt was made to decide, by following the progress of the fusion phenomenon, whether the crystallized substance is chemically homogeneous or whether it contains different crystallized components.

To this end the change in optical anisotropy with change in temperature at constant elongation was studied. Vulcanized threads of rubber were stretched 395 per cent and completion of the resulting molecular rearrangement was awaited. After the double refraction at 20° C had almost reached its final value, the temperature was raised to 40° C and maintained at this point for a considerable time. Finally the temperature was raised to 60° C and held constant at this point. Figure 6 shows that an increase in temperature results in a progressive decrease in the double refraction. The double refraction does not change as long as the particular temperature is maintained constant. When the temperature is lowered, the change in the double refraction was found to be reversible. The temperature was lowered to 20° C and maintained constant at this point. Since rearrangement within the lattice requires a certain length of time, it was necessary to wait for the final value to be reached. The double refraction in-

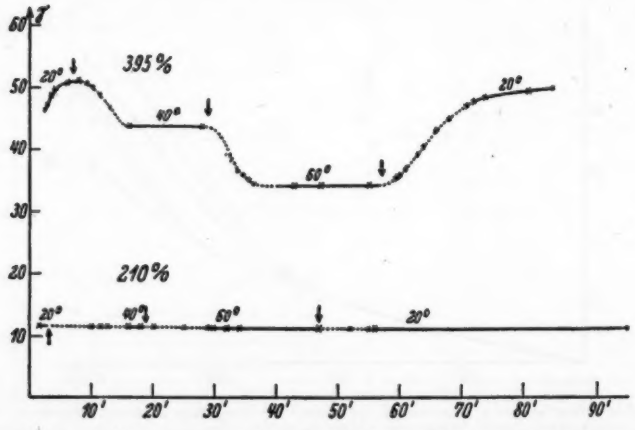

FIG. 6.—Changes in double refraction after rapid stretching and subsequent heating and cooling.

The heavy part of the curves represent measurements at constant temperature; the arrows point to the moments at which heating or cooling commenced. The dotted part of the curves give the measurements made while the temperature was changing. Abscissa=time in minutes. Ordinate=double refraction in Na-light units, based on a thickness of 1 mm. Parameter=percentage elongation and temperature.

creased at a diminishing rate, and reached after a certain time exactly the same value which it had before the heating.

Rubber stretched 210 per cent showed within this range of temperature no change in its double refraction with change in temperature.

Figure 7 gives values of the double refraction as a function of the temperature. As the temperature becomes higher, the double refraction decreases continuously.

To throw further light on the problem, a parallel experiment was made under similar conditions, but this time molecular rearrangement in the lattice was followed by means of x-rays. A comparison of the x-ray diagrams of the rubber at 20°, 40° and 60° C shows that, as the temperature is raised and the double refraction is thus diminished, there is an increase in the halo at the expense of the sharp reflections. In this case also, the change in the x-ray diagram was reversible, *i.e.*, after the rubber threads had been cooled, the sharp lattice reflections recovered the same intensity which they showed before the rubber was heated.

Figure 8 shows x-ray diagrams of rubber, stretched 400 per cent, which were taken at a series of temperatures somewhat different from those of the previous series. Here the specimen, after being photographed at 20° C, was heated to 60° C, was photographed, was cooled to 20° C again, was photographed, and was heated to 40° C. The two x-ray diagrams taken at 20° C are the same; the diagram taken at 60° C shows a much stronger amorphous ring at the expense

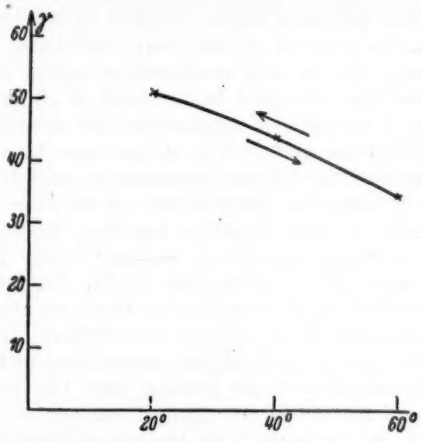

FIG. 7.—Double refraction as a function of temperature.

The values for the double refraction are taken from Figure 6. Abscissa=temperature. Ordinate=double refraction in Na-light units, based on a thickness of 1 mm.

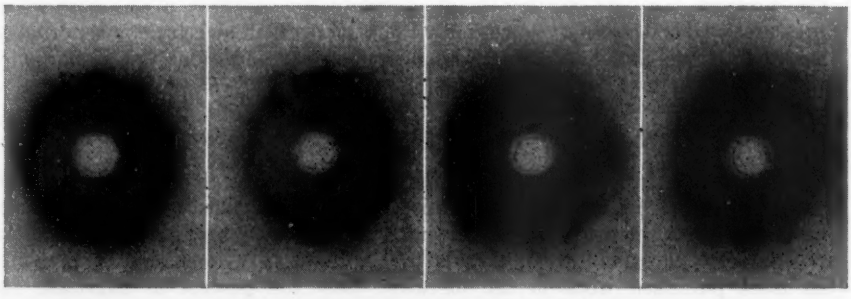

FIG. 8.—Influence of a change in temperature on the x-ray diagram of a vulcanized rubber strip elongated 400 per cent.

The diagrams were obtained with the rubber at 20°, 60°, 20° and 40° C. CuK radiation. Diameter of chamber 57.2 mm. Time of irradiation 30 minutes. The photographs were taken under the same conditions and were reproduced jointly.

of the intensity of the sharp reflections. The x-ray diagram taken at 40° C is of an intermediate character and shows clearly the progressive diffusion of the sharp interferences.

These results lead to the conclusion that, at the same pressure, a definite equilibrium between the crystallized component and amorphous fused component is established at any definite temperature within a wide range of temperatures.

Judged by the manner in which the anisotropy varies with the temperature, it can be concluded that rubber is not a homogeneous substance. A homogeneous

substance would necessarily have a sharply defined melting point. Accordingly with an increase in pressure the temperature at which diffusion takes place might well change; however, this fusion process might not extent over so great a temperature range. In the case of stretched rubber, the large fusion range can be explained most simply on the assumption that the crystals have different melting points. The existence of such crystals depends on the fact that rubber contains various components which differ in their degree of polymerization. These various polymers show a similar basic structure for, with progressive elongation, the position of the sharp reflections which depend on the lattice do not change, nor do new interferences appear in the x-ray diagram. Accordingly the same unit cell must be the basis of all crystals. This condition can be fulfilled only if the different components are constructed of small, strictly similar recurring structural units. It is at the same time possible that in the process of rearrangement the different components unite to form mixed crystals. In this process of crystallization the polymers of the same degree of polymerization would be expected to tend to gather together. Between the crystals which wholly, or to a great extent, consist of the most highly polymerized molecules and those which consist chiefly of the least highly polymerized molecules there are as many intermediate types of crystals as there are stages of polymerization. When rubber is stretched at a constant temperature, the mixed crystal first formed is that richest in the most highly polymerized molecules[23], because long chains rearrange themselves with the greatest ease. On the other hand, on heating, the mixed crystal containing the greatest number of the smallest molecules is the first to melt. At the same time the crystalline phase changes with the temperature according to its quantity and to its composition. In conjunction with the fusion curve of natural rubber obtained by von Susich[24], this leads to the conclusion that the melting point of crystalline rubber depends greatly on the pressure, *i.e.*, its melting point increases considerably with increase in pressure[25] (the degree of elongation). The increase in density[26] when rubber is stretched and also the relatively small heat of crystallization[27] are in harmony with this discovery.

AFTER-EFFECT OF THE MOLECULAR ARRANGEMENT

It is evident from the fusion curves described above that with increase in temperature the proportion of crystallized substance diminishes, but with subsequent cooling it increases to its original value again. The process is therefore reversible. The same reversibility is to be found with a change of pressure. In most published work in the literature only the process of molecular rearrangement has been studied to any great extent. The characteristic property of high elasticity possessed by rubber is, however, not merely its elongation but the complete reversibility of this phenomenon. For this reason the changes in double refraction were followed, not only during stretching but also during retraction.

Rubber thread was stretched at a constant rate to a definite elongation and, after a short interval of time, was allowed to retract at the same uniform rate (see Figure 9). Whereas after relatively small elongations the same double refraction values were obtained during retraction as during stretching, at higher elongations a hysteresis effect was observed, *i.e.*, the value of the optical anisotropy for any particular total elongation was higher during extension than during retraction. When retraction had progressed far enough, the retraction curve approached that of the extension curve and ultimately followed the same course.

It was proved by x-ray examination that in the region of the hysteresis area which is enclosed by the extension and retraction curves, a lattice arrangement is present. At an elongation of 200 per cent there was no perceptible hysteresis (see Figure 10), since at this elongation the formation of a lattice structure still could not take place.

On retraction the lattice arrangement of the molecules could still be observed below the degree of elongation necessary for the formation of a lattice. At first

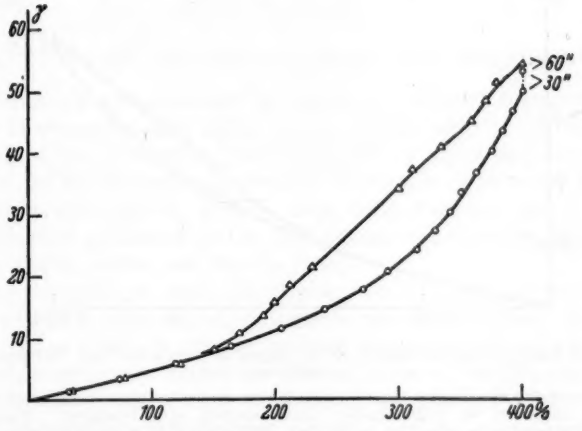

FIG. 9.—Double refraction as a function of the degree of elongation, with uniform extension and retraction.

Stretching required 8.53 minutes (curve marked with circles). After an interval of 1.5 minutes, retracting was completed in 9.83 minutes (curve with triangles). Abscissa=percentage elongation. Ordinate=double refraction in Na-light units, based on a thickness of 1 mm. Temperature 20° C.

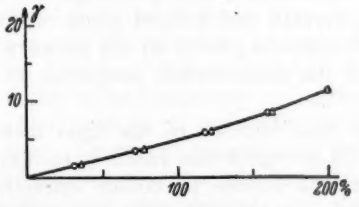

FIG. 10.—Double refraction as a function of the degree of elongation, with uniform stretching to an elongation of 200 per cent and uniform retraction after an intermission of 1.5 minutes.

Extension marked by circles; retraction by triangles. Abscissa=percentage elongation. Ordinate=double refraction. Temperature 20° C.

thought such an observation seems to be at variance with the existence of an equilibrium between the crystalline and fused phases which depends on pressure. However, it must be considered that whether or not this equilibrium is reached depends greatly on the time[28] at which the measurement is made, because the times of the measurements are very short for such a highly viscous system and actually in such a process only an approximate equilibrium is reached unless the measurements are extended over extremely long periods of time. The true equilibrium curve would therefore lie between the two experimental curves shown.

With a reduction in viscosity, *i.e.*, a rise in temperature, the state of equilibrium is necessarily reached more quickly. As a matter of fact, at 40° C a much smaller hysteresis effect was found. Here too the molecular arrangement was of course less developed because of the higher temperature (see Figure 11).

The hysteresis phenomena can likewise be followed by stress-strain measurements[29] and by density measurements[30].

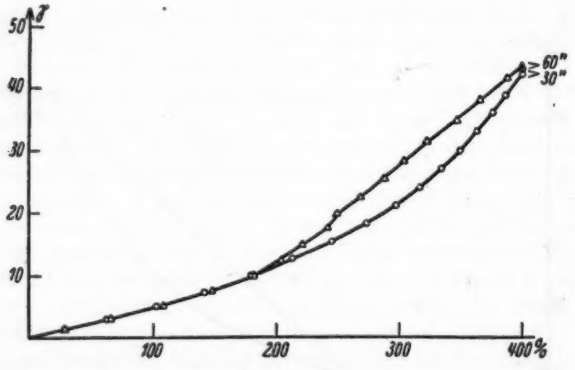

FIG. 11.—Double refraction as a function of the degree of elongation, with uniform stretching and retraction.

Stretching required 8.62 minutes (curve marked with circles). After an interval of 1.5 minutes, retraction was completed in 8.62 minutes (curve marked with triangles). Abscissa=percentage elongation. Ordinate=double refraction in Na-light units, based on a thickness of 1 mm. Temperature 40° C.

RÉSUMÉ

The results obtained in the investigation just described lead to the conclusion that stretched rubber consists of a multiphase system, in which, within a wide range of temperatures, crystals and a fused phase of different compositions are in an equilibrium which depends greatly on the pressure. From this relationship it is possible to explain the characteristic properties of rubber, particularly its wide range of elasticity[31].

In all measurements the influence of the time factor must be taken into account at all times. To disregard this factor is to open the way to erroneous results, and this statement applies to double refraction, density and tensile measurements, to studies of x-rays diagrams and probably also to calorimetric measurements and other thermal studies.

EXPERIMENTAL PART

The relation between double refraction and optical anisotropy can be expressed by the following equation:

$$\gamma\lambda = d(n_1 - n_2)$$

where n_1 and n_2 are the principal indices of refraction, d is the density of the sample, λ is the wave length of the light used for the measurement, and γ is the difference in path in the two planes of vibration perpendicular to one another, *i.e.*, the order of the double refraction. In such an expression, the value of γ

for sodium light represents the magnitude of the double refraction. The values of γ are calculated for every measurement to a basis of 1 mm. thickness to make it possible thus to compare the individual measurements in a simple way. On the assumption that the volume of the test-strip remains constant (the slight change in density is of only minor significance from this point of view) and also assuming a square or at least a nearly square cross-section, it is possible to calculate the decrease in thickness for any elongation. The justification for this method of calculation is supported experimentally by control measurements of the density.

EXECUTION OF THE DOUBLE REFRACTION MEASUREMENTS

Double refraction was measured by means of a Babinet compensator. Examination was in monochromatic light, with a sodium lamp as the source of light. It was not possible to examine thick specimens by white light, since the strong dispersion of the double refraction made it impossible to recognize the zero mark on the Babinet compensator. But by using monochromatic light it was possible to work with thick specimens and at high elongations, since the extinction bands, even of the higher orders, are equally sharp.

When the elongation is rapid the double refraction quickly reaches a certain value beyond which point its rate of increase diminishes to zero. The determination of the value which is reached quickly is carried out by counting off the orders which pass rapidly across the field of vision of the Babinet compensator and adjusting the mark of the compensator on the last graduation so as to follow continuously the slow changes.

Recording of the changes in double refraction was mechanical. A pencil was coupled to the set-screw of the Babinet compensator through cone wheels, cog wheel and rack, so that the pencil marked every change immediately on a drum rotating at a known speed. This contrivance obviated any protracted recording of the readings and made it possible to observe uninterruptedly the strip of rubber without danger of incorrect readings. From the curve which was traced in this way, it was easy to read the value for any time whatsoever. To this value, which was converted to a basis of the fractions of the orders of the double refraction for sodium light, it was necessary to add only the number of the orders passing at the first moment of stretching to obtain the exact double refraction at any moment. Graphical recording of the values makes it much easier to determine the double refraction shortly after rapid stretching. The increase is slower in subsequent measurements and then the compensator can be read directly and the result recorded. With slow elongation, double refraction is measured by determining the time from the beginning of the elongation for the interference band of a certain order to pass through the zero point of the Babinet compensator; likewise the actual elongation as a function of the time is measured periodically. The elongation for each order can be read immediately, by means of time readings, from the elongation-time curve which, with the constant-speed motor, is a straight line.

X-RAY DIAGRAMS

The x-ray diagrams were obtained by photographing the rubber while elongated in a specially constructed chamber. An open Seemann x-ray tube was used,

with Fe and Cu radiations. With the small resolution of the camera and high capacity of the tube, irradiation times of 1 to 2 minutes were sufficient. The x-ray diagrams were taken with Agfa-Laue films.

PREPARATION OF THE SPECIMENS

The material had a rubber content of 93.8 per cent, and was in the form of films approximately 0.5 mm. thick. Strips 2 mm. wide and about 25 mm. long were cut from these films. Strips of this form were chosen because it was then much easier to calculate the elongation in advance than it would have been with test-specimens having enlarged ends for clamping, such as are used in tensile testing. Razor blades were used for cutting the specimens, and to avoid bending they were guided carefully at a distance of 2 mm. apart. Sheet lead was found to be most suitable as a base on which to cut.

To follow the actual elongation, two marks 10 mm. apart were made on each strip. A thread was drawn through by means of a very fine needle, and the thread was then cut off so that its end remained in the rubber strip. This artifice had the advantage over ink marks on the strip in that the distance could be easily measured; the edges of ink marks are usually blurred at high elongations and are too ill-defined to be read clearly.

The objection may be raised that a rubber strip is weakened at these sections and consequently that the sections are necessarily elongated more than is the section actually under observation. A check on this point showed that the elongation was no higher, within experimental errors. A thread was marked with equidistant ink marks and was then elongated. Nevertheless in the spaces which are supposedly weakened by the bits of thread in the rubber, measurements showed the same elongaton as at the sections which had not been punctured. Naturally the fineness of the needle determines whether the error is of any significance.

The thickness of a strip was measured by a screw-micrometer. Since the setting was too insensitive for such a soft material, the rubber strip was moved gently back and forth during the measurement. At the moment when an appreciable elongation is necessary to move the strip, the reading on the screw-micrometer gives the exact thickness of the strip. Only strips of uniform thickness over the entire length, used for the measurements were employed.

In the double refraction measurements it was possible to check the uniformity of the elongation and thickness by ascertaining whether the strip of rubber showed the same double refraction over a considerable longitudinal distance. Only when this condition was fulfilled was it considered proper to make a measurement.

Likewise this check test showed that the effects of the clamping device are confined to a small distance, and with a sufficient length the measurements are not vitiated if they are made in the section between the stretching appliances.

The greatest possible care must be taken in all experiments with the clamping device, for even slight slipping of a sample in the grip makes the whole measurement valueless, since a constant elongation is a prerequisite for precise measurements. The corrugated brass jaws which were formerly used, and which were squeezed together by a screw, were found to be unsatisfactory when a rubber strip was clamped before stretching and was then elongated. When the pressure was too little the rubber slipped; when the pressure was too great the rubber was easily cut. The reason for the rubber slipping out of the clamps is that the thickness becomes much less when the rubber is stretched. For this same

reason, however, a clamped, stretched strip of rubber can be easily held fast by suitable grips.

Nevertheless a rubber strip which it is intended not to stretch before measurements are made can be clamped in the same way by proper manipulation. The clamps are so designed that the end of the rubber strip can be made to project. The strip is stretched, with the screw clamp slightly tightened, until the strip is just on the point of slipping in the clamp. A piece is then clamped while highly elongated, and on stretching the section of this strip which has not previously been stressed, no appreciable slipping in the clamps takes place.

Two forms of clamps were employed, as shown in Figure 12. Both were very satisfactory.

FIG. 12.—Clamping device for rubber threads.

(a) Brass wedge in which the rubber thread is placed and is held tight by pressure between the brass parts.
(b) Two small brass plates, which can be compressed by a bolt, and which have notches filled with lead in such a way that the lead B in one brass plate protrudes and thus presses the rubber thread K against the lead lining of the other brass plate.

The chambers in which the rubber was stretched were provided with supports with the aid of which the grips could be easily inserted and securely fastened.

CHAMBERS IN WHICH RUBBER STRIPS WERE ELONGATED

(*a*) *For Measurements in Polarized Light.* (See Figure 13.)

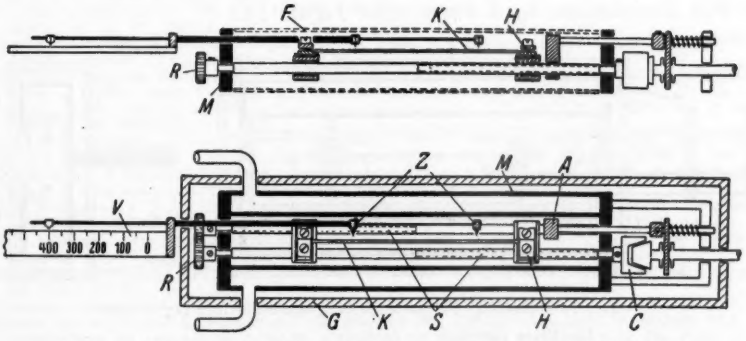

FIG. 13.—Chamber for stretching rubber in measurements by polarized light.

M Brass chamber.
F Glass window.
S Spindle.
R Cog wheel.
H Clamp for rubber thread K.
C Clutch.
A Limit stop for releasing clutch C.
Z Pointer to be set on marks on the rubber thread, and connected with scale V and thus with marks on the scale for checking and measuring the true elongation.
G Housing of Pertinax for heat insulation.

The apparatus consisted of a brass chamber M, the longer sidewalls of which were rectangular compartments. The top and the bottom of the chamber were closed with glass observation windows F.

In the chamber M were two spindles S which could be rotated in opposite directions by coupling through two cogwheels R 1:1. On each of these spindles was a holder for clamps H. One spindle was connected by a clutch to a gear which was driven by an electric motor. When this spindle was turned, the other spindle turned in the opposite direction, and each spindle carried a support for the clamp holding the rubber thread K which moved outwardly, so that, by means of a constant-speed motor, uniform stretching of the rubber was assured. For rapid stretching an additional clutch C was inserted, and this was released when one of the two supports reached the limit stop A. This limit stop A was adjustable, so that the mechanism could be set beforehand for any desired elongation. With this system, a uniform rate of elongation to the final point desired was assured. By stretching the rubber to the same extent in opposite directions, the middle section remained within the field of vision throughout the stretching operation.

In the chamber were also two needle pointers which could be adjusted from the outside and which were placed on the marks on the rubber. One of the pointers was connected with a movable scale, the other pointer with a mark on this scale. In this way the actual elongation to which the rubber had been stretched and its constancy during the measurements could be verified.

The sidewalls, consisting of rectangular compartments, were cooled with water to maintain a constant working temperature or as a means of changing the temperature. The water was driven by a centrifugal pump from a thermoregulator through the apparatus and thence back into the thermoregulator. This sort of temperature control assured satisfactory constancy and made it possible, within a range of about 20° to 80° C, to adjust easily to the particular temperature range within which the measurements were to be made. The entire chamber was enclosed in a Pertinax housing to minimize heat exchange with the surroundings.

(*b*) *For Examination by X-Rays.* (See Figure 14.)

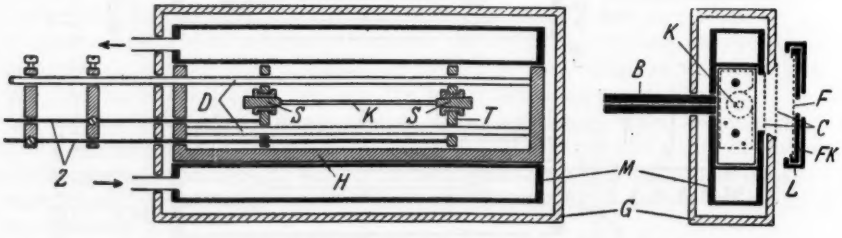

FIG. 14.—Chamber for the stretching operation in x-ray studies.

M Brass chamber.
B Screen.
C Film of Cellophane.
K Rubber thread in clamp and stretching mechanism S.
D Guide wires fastened in supporting frame H.
Z Traction wires.
G Pertinax housing.
L Frame for film box FK in which film F rests.

A brass chamber M, the top and bottom walls of which were rectangular compartments, was equipped, on the middle of the long front wall, with a screen B; on the opposite wall was a window, and this was sealed with a film of Cellophane C. The stretching device could be inserted from the side in such a way that the strip of rubber is automatically located in front of the screen.

The stretching mechanism consisted of two small pieces of brass, each with a slot in which the clamp for the rubber strip K was inserted. These brass pieces were supported by two steel wires D (3 mm. diameter); these wires were in turn held in a frame H. To each of the brass pieces was fastened a wire D, which could be drawn outward and clamped tight.

The chamber was enclosed in a Pertinax housing G for heat insulation. Behind the window was a supporting guide L for the film box FK; this frame could be set at different distances. The frame for the films could be moved horizontally in this guide, so that several x-ray diagrams could be taken one after another on the same film F. Since, with the rubber strip in one position and with the same time of exposure of the photograph plates, all photographs were taken under the same conditions, comparison of the diagrams was greatly simplified. It was also possible to detect with a high degree of certainty, small differences in the character and intensity of the reflections.

ACKNOWLEDGMENT

The mechanical construction of the apparatus and chamber was under the supervision of Erich Franke as technician. We are grateful to him for many suggestions and improvements in the design.

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MECHANICAL PROPERTIES OF "TWO-DIMENSIONAL" RUBBER. THE MICELLAR STRUCTURE OF RUBBER *

A. A. TRAPEZNIKOV

It has been suggested by a number of authors[1] that the enhancement in the mechanical properties of rubber by loading it with active fillers is connected with the transition of the rubber into a special state on the surface of the filler particles. Rehbinder and Margaretov[2], studying the mechanism of activation due to fillers, consider this change in the mechanical properties as a transition of the rubber into a two-dimensional film-state of solvate membranes which, similar to thin liquid layers[3], possess anomalous mechanical properties (elasticity in shear), as well as a peculiar colloidal structure.

In the present investigation the mechanical properties of thin films of rubber were studied with the aim of discovering their anomalies, the appearance of which may be expected for sufficiently thin and, most probably, oriented films.

The mechanical properties, characterized by deformation curves during stretching, were studied with an apparatus consisting of a paraffined trough containing water, on the surface of which was placed a film of rubber, spring balances (glass needle) to measure the tension, and two barriers to stretch the film. One barrier, in the form of a paraffined strip of paper floating freely, was joined by steel hooks to the lower ends of the balance; the other, a glass one, moved along the ends of the trough.

The films were formed by the evaporation of a drop of a toluene sol. However, preliminarily, a layer of palmitic acid[4] was deposited on the water surface. This prevented: (1) the unbounded spreading of the drop of the sol over the whole water surface, and (2) the adhesion of the film to the edges of the vessel (when, in order to obtain very thick films, the vessel employed was of small dimensions). The areas of spreading, determining the thickness of the film (from the weight of rubber contained in one drop), may be controlled by changing the surface concentration of the layer of palmitic acid, which becomes more dense during the spreading of a sol drop up to about a condensed state.

The tension was calculated with reference to 1 sq. cm. of the initial cross-section. The rubber was purified by precipitation with alcohol from a toluene solution, preliminary filtered from pectin substances.

In such a manner films ranging from 25 to 4000 Å. were obtained. For thicknesses greater than 500-800 Å., the films were colored due to interference, while for smaller thicknesses, they were colorless and visible only in reflected light against a dark background. These thin films were porous (veined), which accounts for the comparatively low tension strengths.

Fig. 1 shows deformation curves of rubber films (light crepe) on distilled water for thicknesses ranging from 25 to 3000 Å. It may be seen that the films are divided into two groups: "thick" films, from 300 Å. and higher, and "thin" films, up to 200 Å. The "thick" films give deformation curves similar to those

* Reprinted from *Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS*, Vol. 22, No. 2, pages 83-86 (1939).

obtained in the case of stretching of three-dimensional rubber; they are S-shaped and are characterized by a section of plastic elongation about 500-600% (the total elongation at rupture is 1000-1200%). The "thin" films on the contrary lack plasticity, their deformation curves being almost linear, *i.e.*, the relation between deformation and elongation for this group of films is in close conformity

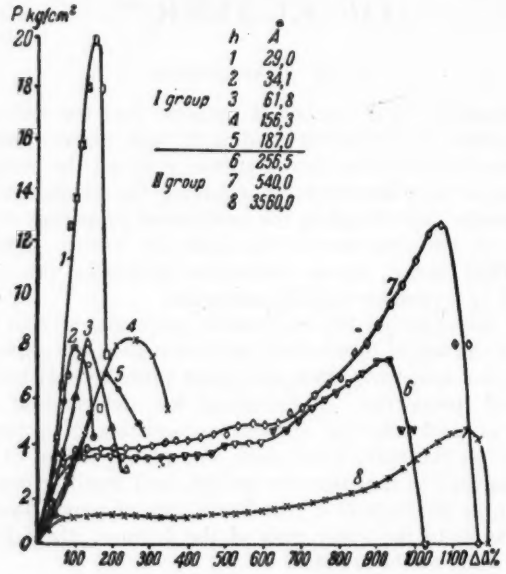

FIG. 1.

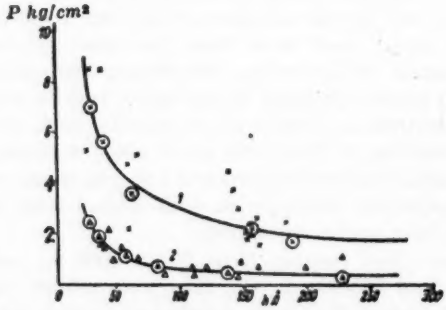

FIG. 2.—*1*, Light crepe on distilled water; 2, Smoked sheet on tap water (Δl=66%).

with Hooke's law. In compliance with this the curves characterizing a drop in the load during contraction of the stretched "thin" films give almost no residual deformation or hysteresis loop, while the hysteresis loop formed by the curves of the contraction of "thick" films is very large and is determined mainly by the amount of plastic elongation. As the films become thinner, the modulus of elasticity increases, as shown in Fig. 2, and complete elongation at rupture decreases from 1000 to 200-300%.

These data corroborate the above assumption concerning the appearance of abnormally high mechanical properties for very thin films of rubber.

An especially sharp qualitative distinction in the mechanical properties is observed in films beginning with a thickness of 200 Å. On further thinning of the film, the character of the curve does not change except to become more steep, *i.e.*, the modulus increases. The appearance of visible porosity in films of these thicknesses (starting with 200 Å.) points to the impossibility of a further homogeneous thinning of the films and to the fact that at these thicknesses a minimum thickness is attained which seems to correspond to the size of a structural unity, for example, to a rubber micelle.

It follows that the difference in the mechanical properties of the two groups of films may be explained in the following manner. In thick films, the rubber

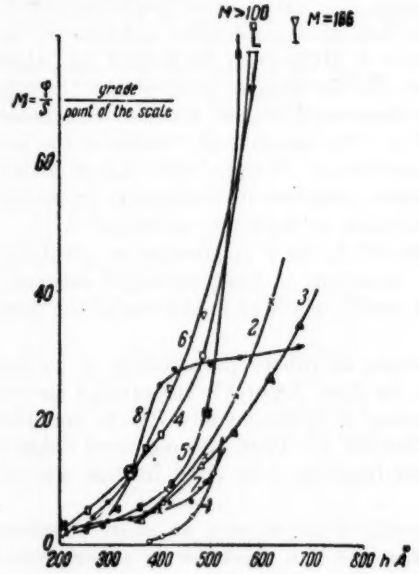

FIG. 3.

Number of curve	Sol concentration	Number of drops induced on the surface	Lining
	LIGHT CREPE		
1	0.078	42	Water
2	0.078	60	0.001 *n* HCl
3	0.078	60	0.001 *n* HCl
4	0.0195	240	0.001 *n* HCl
5	0.078 + 5% of palmitic acid	55	0.001 *n* HCl
6	0.156 + 2.5% of palmitic acid	30	0.001 *n* HCl
7	0.078 + 5.2% of cetylic alcohol	55	Water
	SYNTHETIC CAOUTCHOUC		
8	0.127	40	0.001 *n* HCl

micelles, after evaporation of the solvent, remain in a state of chaotic interweavement and the plastic region of expansion corresponds to the slip and gradual orientation of micelles. However, in thin films, owing to the drop being spread over a large area, the micelles arrange themselves in one layer with a definite orientation which excludes their plastic slip past one another. As the thickness of the film decreases, the orientation conditions become better, which leads to an increase in the modulus of elasticity. Two-dimensional rubber is equivalent to three-dimensional «crystallized» rubber.

Owing to the porosity of the thin films, their actual thickness is somewhat greater than the average, and it may be determined by condensing the film (eliminating interspaces), for example, by means of slight compression by blowing. However, from solutions of very small concentrations of rubber, complete films are not obtained, but after evaporation separate unconnected islets remain. By bringing together and condensing such islets, a value of the limiting thickness

also may be obtained. The value $h=360$ Å. was obtained, by this method of blowing, for sol concentrations from 1.42 to 0.07%.

For high concentrations (0.5-1.42%) the values of h may lack accuracy, because of incompletely uniform spreading of concentrated solutions; but the fact that for dilute solutions (even to C=0.02%) homogeneous disintegration (division into small parts) of micelles does not take place, is corroborated by the data of the measurement of the modulus of elasticity for shear by the method of twisting a disc in the film which is suspended on an elastic thread[5]. Fig. 3 gives curves of the dependence of the modulus (in degrees of revolution of the upper end of the thread per one division of the scale during the shift of the light beam) on the thickness of the film during its compression (condensing of the islets) by the barrier on the surface of the water in the trough. All the solutions, from 0.15 to 0.02%, in spite of the incomplete homogeneity of the films, give a sharp increase in the modulus at a thickness of about 400-500 Å. (Curves *1, 2, 3* and *4*). The introduction of surface-active substances, for example palmitic acid (measured on 0.001 *N* HCl), into the rubber sol, which accelerates the spreading of a drop and aids the disintegration of the film into separate micelles, does not change the limiting values of the film thicknesses (Curves *5, 6* and *7*) lying from 350-500 Å. This undoubtedly points to the fact that this value of the thickness is not accidental. Palmitic acid (2.5 to 5.0%), which aids in making the films homogeneous, enhances its mechanical properties. Synthetic rubber gives films having a thickness of the order of 300-350 Å.

The values of the thicknesses, $h=400$-500 Å., may apparently be attributed to the length of the chains in a micelle. According to Hengstenberg's[6] exograms, crystallites in stretched rubber possess a length, width and thickness of the order of 600, 500 and 150 Å., respectively.

Preliminary data obtained with fractions of rubber prepared by a method of fractional precipitation with alcohol (in Prof. Lipatov's laboratory) showed that the film thickness of the first fraction is approximately 700 Å. and that of the second fraction approximately 400-500 Å. Thus, the indicated value is the mean value for a mixture of polymer homologs (the third fraction was not investigated).

These data may be considered as a result of the micellar structure of rubber in solution. For isolated macromolecules, the film thickness in a compressed condition should have amounted to either 4000-8000 Å. for vertical orientation, or to 2.5 Å. for plane location of the chain. The film could have been homogeneously thinned to thicknesses considerably less than 200-400 Å. However, the assumption of any arbitrary average distribution (interweaving) of chains, giving a thickness of 500 Å. for solutions of various concentrations (in the region sol solution at C<0.1-0.24%) and spreading with a different speed, is but very slightly probable. However, thicknesses of the order of 2.5-3.0 Å. may be obtained only under the influence of a considerable stretching force, for example, by a high two-dimensional pressure the surface of mercury. Films on mercury, after evaporation of the toluene, continuously spread to a thickness of 2.5 to 3.0 Å., below which the film loses coherence (qualitative experiments of the adhesion of a film to a rod). The loss of coherence at 2.5-3.0 Å. evidently corresponds to a gaseous structure of the monolayer with the disintegration of micelles to separate, flatly lying, not touching chains. This agrees with Keenan's results[7]. The results of an electron-diffraction analysis of thin ($<10^{-5}$ cm.) films of rubber on water[8] show that they are oriented (crystalline).

The method of monolayers may be adapted to colloids in spite of the formation of islets, since at corresponding conditions the structure of the given islets is sufficiently definite; they are two-dimensional micellar aggregates, formed during the process of evaporation of the solvent.

This investigation, which was started in the Laboratories of the Liebknecht State Pedagogical Institute, is being continued in the Department of Physical Chemistry of Disperse Systems of the Colloidal Electrochemical Institute of the Academy of Sciences of the USSR.

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THE CHEMISTRY OF NATURAL RUBBER *

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UNITED STATES RUBBER PLANTATIONS, BOENOET, KISARAN, SUMATRA, EAST COAST

Roberts (*J. Chem. Soc.*, **1938**, 215, 219) dissolved air-dried films from fresh latex in acetone-carbon tetrachloride and coagulated the solution by the addition of further acetone; the supernatant liquid contained an ingredient which was soluble in ligroin, contained sulfur, might be elastic, and was termed by Roberts, *caoutchol*.

Roberts stated that removal of this caoutchol ingredient caused marked changes in the properties of the remaining rubber, "characterised by its lack of tensile strength and the remarkably low viscosity of its solutions." This rubber was dried in air for 24 hours, dissolved in benzene, centrifuged, and emulsified with water and the benzene removed by steam distillation. The rubber remaining was tacky and feebly elastic after drying in a vacuum, and was termed *caoutchene*.

Roberts developed the theory that the elasticity of crude rubber is due to the presence of caoutchol and that, without caoutchol, rubber has very poor elasticity and low viscosity in solution.

Insufficient attention has been paid to the role of oxygen in the purifications described. Roberts states: "The process has been carefully examined, particularly with respect to the possibility of oxidative or other changes in the constituents. No evidence of such changes has been obtained." Yet the coagulated rubber, after removal of the caoutchol but prior to steam distillation, was milled in air, and dried in air for 24 hours, during which time considerable oxidation could have occurred.

The following analysis of caoutchene is given: C, 87.0; H, 11.8; N, 0.5; S, 0.1; O (by difference), 0.6%. The oxygen content is stated to be equivalent to the nitrogen content, since the two occur in the same ratio as in most proteins, and therefore the oxygen found by difference is assumed to be protein oxygen, and not combined with the hydrocarbon. This assumption is not necessarily justified, in view of the error inherent in estimating oxygen by difference from combustion-analysis results of carbon, hydrogen and sulfur, which is large relative to the low value of the nitrogen found. It must therefore be concluded that the analysis given does not constitute a proof that oxygen has not been taken up by the hydrocarbon in the caoutchene fraction during its preparation.

We prepared rubber free from the caoutchol fraction and found it to be elastic and non-tacky if sufficient precautions were taken to conduct the purifications in oxygen-free nitrogen. Fresh latex, an hour old, was coagulated by running it into 95% ethyl alcohol, to avoid any possible bacterial changes which may have occurred in Roberts's procedure of relatively slow air-drying. The coagulum was pressed and vacuum-dried to a moisture content of 0.15%. The dry rubber was dissolved four times in dry carbon tetrachloride-acetone under oxygen-free nitrogen and precipitated four times by the addition of further dry acetone, approximately Roberts's proportions of solvents being used. This solution and precipitation procedure for the removal of caoutchol, Roberts carried out only once. The final precipitate of rubber was freed from solvent in a vacuum, milled thin and dried in a vacuum over sulfuric acid, the air in the desiccator

* Reprinted from the *Journal of the Chemical Society*, April 1939, pages 676-677.

having been replaced by nitrogen before evacuation. The dry piece of rubber so obtained was not tacky and was quite elastic as determined in the hand. It began to show tackiness after 24 hours' exposure to air.

This experiment with dry rubber and solvents fulfils Roberts's specification, given in a private communication, that the removal of caoutchol from rubber is complete only in the absence of moisture. The removal of caoutchol from rubber does not lead to tackiness and loss of elasticity. These properties appear when caoutchol-free rubber suffers oxidation, but do not appear if oxygen is excluded from the rubber, during or after its preparation.

THE CHROMATOGRAPHY OF RUBBER SOLUTIONS *

GIAMPIETRO CAJELLI

MARCA AEROPLANO S. A., MILANO, ITALY

In the opinion of Pummerer, there is considerable doubt about the homogeneity of the fractions obtained by fractional precipitation of rubber from dilute benzene solutions, both with respect to the size of the molecules and to the state of aggregation. Based on the results of x-ray measurements of fibrous substances, to which type stretched rubber belongs, Meyer and Mark have advanced the hypothesis of the existence of chains of primary valences and of a micellar structure.

PURIFICATION OF RUBBER

There are four important and at the same time essentially different ways of carrying out the difficult process of purifying rubber. According to Harries, acetone extraction gives a colored product and leads to profound changes in the elastic properties. Staudinger[1] adopted the method described by Wildmann in 1911, which involves the use of a mixture of acetone and chloroform. On the other hand, Pummerer and Koch[2] used the method of fractional precipitation; the rubber after severe mastication was extracted with acetone, was dissolved in benzene, the liquid was allowed to stand for several weeks, the solution was decanted from the insoluble residue and was fractionally precipitated by alcohol and acetone. More recently this same method has been perfected by Pummerer and Meidel[3], and by this means a fraction of crystallized rubber was isolated from the mother liquors of the fractional precipitation.

Finally Pummerer and Koch have purified rubber by treatment with an alkali, combining the precipitation method with the use of a solution of potassium hydroxide in methanol. Later this method was modified by Pummerer and Pahl.

The use of latex in place of crude rubber is the most important development in obtaining a satisfactory product. De Vries and Beumée-Nieuwland[4] have described in detail some results obtained with fresh latex.

The total-rubber obtained by the methods just described contains, according to the quality and the age of the sample of latex, from 0.1 to 0.4 per cent of nitrogen which cannot be removed by washing, even when this is exhaustive.

SOLUTION OF PURIFIED TOTAL RUBBER

There is at present no satisfactory method for the separation, by means of a precipitating agent, of nitrogenous impurities from a rubber solution, and it is preferable to separate these impurities by the reverse process, *i.e.*, by fractional solution of the rubber. With their total-rubber, Pummerer and Pahl studied the question of the sol and gel phases, and they were able to remove, by means of ether, about two-thirds of the product, leaving as the other third a residue of gel rubber. The reciprocal transformations of gel rubber to sol rubber and

* Translated for *Rubber Chemistry and Technology* from *Gomma*, Vol. 3, No. 1, pages 1-7, January-February 1939.

sol rubber to gel rubber were the subject of later investigations by Pummerer[5]. It was found that even a trace of nitrogen plays an important part in the formation of the ether-insoluble phase, and that the insolubility of gel-rubber in ether increases as aging progresses.

MEASUREMENTS OF THE VISCOSITIES OF THE EXTRACTS OF CHROMATOGRAPHIC ADSORPTIONS

The experiments which are summarized below were carried out by G. R. Levi in collaboration with H. Ottenstein, and they are purely of orientative character, although there was no lack of care taken in their execution. The reason for this reserved statement is that, according to the earlier experiments, the total-rubber was not, in our opinion, of sufficiently great purity, as will be more evident from the experimental work to be described.

The viscometric measurements were carried out in an ordinary Ostwald viscometer, and are expressed as η_r values, as in the earlier chromatographic experiments of Levi[6].

First Experiment.—The solution employed was a 0.5 per cent solution of total rubber in a mixture of 80 parts of benzene and 20 parts of 95° alcohol. The rubber was first dissolved in benzene and this solution was diluted with alcohol; 250 cc. of the resulting solution was chromatographed on 30 grams of well dried animal charcoal (Merck), the animal charcoal was then washed with 250 cc. of a benzene-alcohol mixture of the same composition. This procedure required altogether about ten hours. The mass of animal charcoal, without being allowed to become dry, was divided into three approximately equal parts, and each part was extracted in a Soxhlet extractor with a mixture of equal parts of carbon disulfide and carbon tetrachloride. After cold evaporation in a vacuum, the three parts were dissolved separately in carbon tetrachloride to make 0.5 per cent solutions, and the viscosities of these solutions at 20° C were measured. The results were as follows:

Sample	Viscosity (η_r)
1st aliquot part	1.027
2nd aliquot part	1.002
3rd aliquot part	1.001
Filtrate	1.071

Second Experiment.—The same procedure was used as in the first experiment, but in this second series the concentration of the original solutions and also that of the extracts was 1 per cent; the temperature was 22° C.

Sample	Viscosity (η_r)
Original solution	1.131
1st aliquot part	1.102
2nd aliquot part	1.076
3rd aliquot part	1.055
Filtrate	1.082

Third Experiment.—The procedure was exactly the same as that in the second experiment, except that the adsorbent was washed with only 25 cc. of a mixture of benzene (70 parts) and 95° alcohol (30 parts) and then with 25 cc. of a mixture of benzene (60 parts) and 95° alcohol (40 parts). The final viscometric

measurements of the extracts were carried out in 1 per cent carbon tetrachloride solutions at 22° C.

Sample	Viscosity (η_r)
1st aliquot part	1.117
2nd aliquot part	1.088
3rd aliquot part	1.068
Filtrate	1.072

In still another experiment procedure followed in the third experiment was repeated; but with a double washing, *i.e.*, with 50 cc. each time. In this case the yield of adsorbed rubber was 91 per cent; the yield from the filtrate was 9 per cent.

These preliminary experiments showed that chromatographic fractionation took place and that the viscosities of the extracts from the chromatographs decreased progressively; the viscosity of the filtrate was relatively high compared to the viscosities of the individual portions of the adsorbed product and was of the same order of magnitude as the viscosity of the middle part, but in each case higher than that of the last portion. The results of the first experiment are to be accepted with reserve, particularly because of the high dilution.

EXPERIMENTAL PART

The Method Used for the Preparation and Purification of Total-Rubber

As has already been mentioned, the methods which have been described do not, in our opinion, give a product of sufficient purity. We were therefore led to develop a method which would give a rubber which would be physically as nearly as possible identical to the original rubber but which would show by analysis a composition conforming to C_5H_8. A product of this character should be perfectly soluble in benzene, which is the solvent best adapted to viscosity measurements in an Ubbelhode viscometer, and should not contain the two phases, sol and gel, already described.

The method used by the present authors is based on the following three processes.

(1) *English Patent 363,193.*—Three per cent of sodium hydroxide, based on the rubber, is added to latex of 35 per cent concentration, the mixture is heated at 90-100° C for 7 hours, after cooling it is diluted to a rubber content of 35 per cent; 30 per cent by volume of a 1 per cent zinc chloride solution is added; the fine coagulum is separated from the aqueous liquor, is washed several times and finally is dried. The nitrogen content of the final product is less than 0.05 per cent.

(2) *The method of Smith, Taylor and Wing*[7].—The latex is dialyzed, 3 per cent of sodium bicarbonate is added, the mixture is digested with trypsin at 38° C for 10 hours, is cooled, 2 per cent of sodium hydroxide is added to aid in the formation of a cream, the upper layer is separated from the lower layer, the lower layer is discarded and the creaming operation is repeated several times; finally the liquid is dialyzed until it is strictly neutral, the rubber is coagulated, and the coagulum is washed and dried at room temperature in a vacuum.

(3) *The method of Whitby, Evans and Greenberg*[8].—This procedure is concerned only with elimination of the resins. It has already been mentioned that

it is not sufficient merely to obtain a chemically pure rubber but that it is also essential that the colloidal properties of the rubber change to the least possible degree during the treatment. Elimination of the resins with hot acetone involves no particular difficulties, but the temperature necessary is so high that colloidal changes are inevitable. To overcome this difficulty, Whitby, Evans and Greenberg carried out their experiments at room temperature, using a mixture of acetone (7 parts by volume) and petroleum ether (3 parts by volume), renewing frequently the extracting liquid. Petroleum ether has a softening effect on the rubber and therefore facilitates penetration of the acetone, in spite of its having no solvent action.

The method used by the present authors, which will be described in detail, was a combination of the three methods described above. The temperature was never allowed to rise above 38° C. The starting material was *Hevea brasiliensis* latex of 60 per cent concentration, which was preserved with ammonia and was one year old. It was diluted with distilled water to a rubber content of 38 per cent. All operations were carried out with exclusion of air, *i.e.*, in an atmosphere of nitrogen.

400 cc. of this 38 per cent latex was placed in a one-liter flask provided with three openings, a central one and two on the side. A glass stirrer with an ordinary seal, filled however with water instead of mercury, passed through the central opening. The stirrer was kept in very slow motion, and a slow current of nitrogen was passed through the latex to expel all air which entered during the various preliminary operations. The nitrogen was introduced through one of the side openings and, after bubbling through the latex, passed out through the other side opening. Nitrogen was bubbled through the latex for one hour.

In one of the two side openings was a stopper through which passed two glass tubes, each provided with a stopcock. Both tubes were connected to the nitrogen cylinder, which was equipped with a reducing valve. The tubes were of different lengths; the inlet tube continued to the bottom of the flask and at its lower end was bent to an L-shape so that, with the slow movement imparted to the latex by the stirrer, the current of nitrogen was blown uniformly through the mass. The end of the outlet tube was on the contrary several centimeters above the surface of the liquid.

After the latex had been sufficiently aerated with nitrogen, the stopcock of the outlet tube and that of the inlet tube through which the nirogen entered were closed; the stopcock of the shorter glass inlet tube was opened so that a current of nitrogen could pass through. The inflow of nitrogen was then increased so that when the stopper holding the stirrer was loosened, an appreciable current of nitrogen was emitted. The opening for the agitator was then quickly closed with a tight stopper, and the current of nitrogen was shut off.

After these preliminary operations, the latex was dialyzed with a view to eliminating ammonia and all other water-soluble substances. A dialyzer of the Gutbier type, with a capacity of 2 liters and with a Cellophane membrane, was used. The top of the removable part was changed somewhat to render it more adapted to the particular conditions; first of all the attachment for the internal agitator was removed and the opening was closed. Instead four new orifices were added, one as an inlet for nitrogen, another as an outlet for nitrogen, still another for introducing the latex and finally one for a purpose which will be described later.

The next operations were carried out in the following way. A strong current of nitrogen was passed into the Cellophane cup for fifteen minutes and then,

while still maintaining this current, the inlet for the latex was connected with the tube of the flask which had served as an outlet for the gas. The connection for the nitrogen on the dialyzer was then broken, and the nitrogen cylinder was connected again to the short glass tube which, as already mentioned, ended above the surface of the latex. The liquid was thus forced into the Cellophane cup without coming into contact with air at any time. When the liquid was completely transferred, all connections were closed, and dialysis was started.

The internal stirrer was removed because its motion would have brought about coagulation of the latex. As a means of promoting dialysis, the Cellophane cup was given a gentle rotary movement. The water on the outside was changed every two hours, and the dialysis was continued until 1 cc. of 0.02 *N* hydrochloric acid was required to neutralize the liquid. This required an average of 24 hours.

The ammonia was not completely eliminated, for if this were to be done it would be impossible to avoid partial coagulation. To operate thus and yet to avoid coagulation is perhaps the most delicate of all the various manipulations.

In the fourth opening of the dialyzer, mentioned above, was a stopper through which passed a glass tube. This tube extended to the bottom of the Cellophane cup and, outside the cup, was provided with a stopcock. When dialysis was complete, the cup in the dialyzer with its four-hole stopper was removed, the stopcocks of the four tubes were closed and the cup was turned upside-down. The fourth opening was then connected with the supply of nitrogen; the stopcock which had first served as an outlet for the gas was opened, and connected with a new flask of five-liter capacity which, like the first flask, was provided with an inlet and an outlet for nitrogen, with an opening for a stirrer and with a fourth opening for introducing the samples. This flask also was graduated on its side to show its capacity, and at the bottom was a vertical glass tube with a stopcock.

After the latex was transferred in the usual way, care being taken that it flowed down the walls so as not to entrap air, a current of nitrogen was passed through the system, and enough water was added (again allowing the liquid to flow down the walls) to make up the dialyzed latex to 2500 cc. The concentration of the latex was thus lowered to about 7 per cent. Then 80 grams of sodium bicarbonate in the form of a 3 per cent solution were added, and the mixture was agitated very cautiously, maintaining an atmosphere of nitrogen throughout the operation and keeping the system in a thermostat at 38° C. A fifth opening carried a thermometer.

After 3 hours at 38° C, an aqueous solution of trypsin containing 2 grams of active enzyme was added: A product with a proteolytic power of 1:400, furnished by l'Industria Chimica Prodotti Estrattivi Animali Negroni of Cremona, was used.

After the trypsin had been added, with slight agitation and still in an atmosphere in nitrogen, the thermostat was maintained for 20 hours at 38° C, and was then cooled to 18° C, maintaining the mixture in an atmosphere of nitrogen and still agitating it slightly.

At this point a solution of 3 grams, *i.e.*, 2 per cent of the weight of the rubber, of sodium hydroxide was added, the mixture was stirred for several minutes, the stirring was stopped, and the mixture was allowed to stand in an atmosphere of nitrogen so that the latex would cream. After 8 hours the stopcock at the bottom was opened, and the under layer was drained off to the line of creaming.

The cream was treated in the same way with alkali four times in succession, after which treatment the cream was washed six times with water, the mixture

being allowed each time to stand for six hours and the water being drained off through the stopcock at the bottom.

After all washing operations had been completed and after having removed the water for the last time, the volume of the resulting cream was read on the graduations on the side of the flask; this was found to be 780 cc., corresponding therefore to a concentration of rubber of 19 per cent.

Finally the cream was diluted to 1500 cc., which corresponded to a concentration of 10 per cent, and the liquid was then transferred to the Cellophane cup by the same procedure already used for the previous dialysis. The sample was then dialyzed again until the liquid was completely neutral. This operation required 36 hours, and during this last dialysis a part of the latex coagulated.

After this, the latex was again transferred to the five-liter flask by the same procedure as before, observing the usual precautions, and was then diluted with an equal volume of water so that the rubber content was lowered to 5 per cent.

To the contents of the flask were then added, at room temperature, 900 cc. of a 1 per cent zinc chloride solution and the mixture was stirred gently. This treatment formed a fine coagulum, from which the water was separated by the stopcock at the bottom, and was washed several times.

Alcohol was then added to the flask until the coagulum was completely wetted, the coagulum was then allowed to stand in the alcohol for 48 hours and finally was removed from the flask and dried in a vacuum to constant weight.

At this point, as shown by the present experiments, the rubber commenced to be appreciably affected by light. For this reason the desiccator containing the coagulum to be dried was protected from light, and in the later experiments care was taken that both oxygen and light were excluded.

After drying, the rubber thus obtained was removed from the desiccator, taken to a room lighted by a feeble red light and passed three times through a small laboratory mill with cold and tight rolls to obtain a very thin sheet.

By following the precautions which have been described, any changes in the rubber were reduced to a minimum; the sheeted rubber was rolled up in tin foil and placed in a Soxhlet extractor to remove the last traces of resins by a mixture of acetone (7 parts) and petroleum ether (3 parts), which was circulated for 40 hours at room temperature (18° C), with complete protection from light. Finally the residue was placed in a vacuum desiccator and brought to constant weight.

The product obtained in this way was the total-rubber which was used for the chromatographic experiments. Its physical appearance was very much like that of ordinary pale *Hevea* crepe, except that it was more nearly transparent and its color was paler. It was fairly elastic and when heated it became sticky.

The product had a much higher dielectric constant than that of ordinary rubber, and when stretched more than 80% it gave the same x-ray fibre diagram as that obtained with ordinary rubber.

Chemical analysis (semicroanalysis) gave the following percentage composition:

	Carbon	Hydrogen
Calculated for C_5H_8	88.15	11.85
Found	88.63	12.14
	87.86	12.07
	87.97	12.06
	87.84	11.76
	88.46	11.98
	89.01	11.63
Average	88.29	11.94

Determination of nitrogen by the semimicro apparatus gave the following percentages:

	Micro Dumas	Micro Kheldahl
	0.0046	0.0045
	0.0052	0.0093
	0.0038	0.0068
Average	0.0045	0.0081

The analyses show that the product conformed to the desired standard. It was preserved in alcohol and in darkness.

Solution of the Purified Total-Rubber

In all experiments, great care was taken to keep the rubber and its solutions protected from light and from heat. The first step was to prepare a solution of total-rubber. After having tried various individual solvents and mixtures of solvents, benzene was chosen as particularly suitable, and with it extremely clear solutions were obtained.

The dried rubber was sheeted out very thin on a small mill in darkness, was cut into very small pieces and these were kept under alcohol, after two days or more in alcohol the rubber was kept for one week in a vacuum desiccator. Ten grains were then placed in a weighed glass bottle, with ground-glass stopper (provided with a thermometer) which remained tight even under pressure.

After having added the rubber, the required volume was made up with pure benzene and the stopper carrying the thermometer was inserted. The bottle was also provided with a steel protective casing. This casing held a stirrer which imparted a gentle movement to the bottle, with the pivot at the top of the neck of a bottle so that the bottom of the bottom followed a circular path in its motion. This scheme was found to play an important part in the operations, because in preliminary experiments it was noted that with irregular agitation thin films of rubber formed on the stopper and on the thermometer, and since this rubber was not in continuous contact with solvent it could be dissolved only with great difficulty.

In addition to the opening for the thermometer, the neck of the bottle had two other openings, which served as inlet and an outlet for nitrogen. When all air had been replaced by nitrogen, the stopcocks were closed and the bottle was set in motion. Glass resistant to the pressure of benzene vapor at 50° C in the thermostat was used, for solution of the rubber was greatly facilitated by heating at this temperature.

At the end of eight days a very clear solution was obtained, but the bottle was agitated for ten days more, so that a perfect solution was obtained.

The homogeneity of this solution was tested in two different ways.

In ultraviolet (Wood) light the effect was similar to that of a ground-glass plate irradiated with intense violet light; no luminescent spots or strata of any kind were visible, even when portions were removed after various times. Samples of the same solution were removed at intervals of 20 to 25 days, and these samples were protected from light, air and heat.

In a second series of tests, samples were removed and their viscosities measured. Here the differences were never greater than 2 seconds for samples which differed both in position and in time. It was decided therefore that the solution of rubber in benzene prepared as described was satisfactory for the purpose.

Viscometric Determinations of the Extracts and Filtrates Obtained in the Chromatographic Adsorption Experiments

In the present work the best solvent was found to be benzene and the best adsorbent was animal charcoal (Merck analytical grade). The charcoal had to be dried for a long time (4 weeks) over phosphoric anhydride in a vacuum desiccator to eliminate all moisture. A glass tube was used for the chromatographic measurements; it was open at the top and had a round bottom to which was attached a tube of small diameter. A porous glass disc was fixed near the bottom, and above the rounded part, of the chromatographic tube. This tube was made by Schott and G. of Jena, and the authors express here their appreciation for such kindness in meeting their requirements. A thoroughly dried asbestos filter was placed on this porous glass disc, and on this filter was placed a compact wad of glass-wool. On top of this glass-wool was placed a stainless steel screen disc which was in perfect contact with the walls of the tube so that its base, on which was placed the column of animal charcoal, rested in a horizontal position. The powdered charcoal was prevented from getting below the screen by two round pieces of closely woven silk cloth.

The tube was 30 mm. in diameter and approximately 300 mm. long; and was capable of withstanding an internal pressure of 2.5 atmospheres.

In each experiment 30 grams of animal charcoal (Merck) were used; this was put in the chromatographic tube by means of a paper cup after the filtering system had been carefully placed in position, as already described. The paper cup was removed gently, and the column of charcoal was gently compressed by tapping. A stopper with five holes was then placed in the upper mouth of the tube. One hole in the stopper served as an inlet for nitrogen, another hole acted as a safety valve, another carried a stopcock for releasing the pressure, still another for a funnel and the final one carried a small tube which was connected with a manometer.

When an experiment was started, the stopcock of the supply cylinder, the discharge tube and the safety valve were kept closed, and a current of nitrogen was passed through the inlet tube. The entire system was then connected, by means of the tube at the bottom, to the stopper of a vacuum-distillation flask, and the carbon was compressed by starting a vacuum below and increasing the pressure above.

After three days the pressure over the charcoal came to equilibrium at 0.5 atmosphere, but the current of dry nitrogen was continued for three more days, with maintenance of a vacuum at the same time. The current of nitrogen was then stopped by slowing down the operation of the vacuum pump, shutting off the inflow of nitrogen and allowing the nitrogen to discharge slowly by itself.

In this way the powder remained more or less intact and its depth increased only 3 mm. The resulting height of the charcoal column was 74 mm. The tubular system over the tube was naturally so arranged that the same pressure could be maintained over the loaded cup as in the chromatographic tube, so as to allow the liquid to descend through the tube itself.

After the charcoal was compressed, the stopcock of the tube was closed, and it was filled with the desired quantity of liquid to be chromatographed. Nitrogen was introduced under pressure at the top while the tube was under no pressure. The end of the loaded cup was inclined and rested against the walls of the chromatographic tube so that with a little skill in manipulating the stopcock the column of charcoal was not affected by the descending liquid.

When the chromatographic tube was filled, the stopcock for loading was closed and the chromatograph was put under pressure, which was gradually increased to 2 atmospheres and maintained constant at this point. In this way the column of charcoal gradually became wet throughout and filtration commenced.

The filtrate was collected in a flask, the stopper of which was connected with the bottom of the chromatographic tube. The whole system was maintained at 18° C and protected from light. In each experiment a volume of 250 cc. of a 1 per cent benzene solution was chromatographed.

Because of the relatively small capacity of the chromatographic tube, it was necessary to refill it three times, and when the first portion of liquid was nearly filtered and before the surface of the charcoal was exposed, the inlet for the nitrogen was opened to the upper part of the loading funnel so that more liquid could flow in. The chromatographic tube and also the loaded cup were wrapped in black paper, with 2 small vertical slots, so that the levels of the liquids could be observed.

The chromatography of 250 cc. of solution required an average of nine hours.

When all the solution had passed through, and in every case before the charcoal had become exposed, the chromatograph was washed three times with 250 cc. of pure benzene by the same technique used with the solutions. This washing required about seven hours. Finally the pressure was gradually lowered, the upper part of the system was removed, the chromatographic tube was stored in darkness for later experiments, and the filtrate which had collected in the flask was evaporated to dryness in a vacuum desiccator. This required about ten days.

In each case a 2.500 gram sample of purified total-rubber was used, with 250 cc. of original solution; 0.440 gram of rubber remained in the flask, *i.e.*, 82.4 per cent was adsorbed and 17.6 per cent filtered. These values correspond to an adsorption a little lower than that recorded by Levi and Ottenstein (*loc. cit.*), although the washing was more thorough.

The chromatographs, *i.e.*, the animal charcoal which had adsorbed both benzene and rubber, were removed while still wet from the tube by forcing a current of nitrogen in at the bottom; in this way the entire cylindrical mass of carbon was removed without cracking it. This was divided into three parts, the top part hereafter being designated as the first part, the middle part as the second part, and the lower part as the third part.

Each part was placed in a filter cup in a Soxhlet extractor. The extracts were kept for 8 days in a vacuum desiccator in darkness, as a result of which all three parts became powdery.

The extractors were then removed from the desiccator and mounted on the flasks; a mixture of equal parts of carbon disulfide and carbon tetrachloride was prepared and the various portions were siphon-extracted cold and in red light. After six days' extraction the three portions were filtered on small funnels, the small residues were washed repeatedly and each filtrate was kept in a vacuum desiccator for eight days. In this way the three tared flasks became coated with films of extracted total-rubber. The dried residues weighed as follows:

First portion	0.832 gram
Second portion	0.361 gram
Third portion	0.196 gram
Filtrate	0.440 gram

Hence approximately two-thirds of the adsorbed material was recovered by extraction. To these same tared flasks benzene was added in sufficient quantity

to make 1 per cent solutions, *i.e.*, 83.2 grams to the first flask, 36.1 grams to the second flask, 19.6 grams to the third flask and 44.0 grams to the filtrate. The solutions were prepared in the standard way already described.

The viscometer employed was that of Ubbelhode; the thermostat temperature was 22° C.

The first measurements were made almost as soon as the solutions were prepared.

First series	Time (in seconds)
Solution to be chromatographed	86
First extract (see above)	90
Second extract	76
Third extract	61
Filtrate	78

After these measurements were made, the flasks were closed tight, placed in darkness and kept in a thermostat for 28 days at 22° C. They were then removed and tested a second time, with the following results:

Second series	Time (in seconds)
Solution to be chromatographed	85
First extract	87
Second extract	74
Third extract	60
Filtrate	77

The data show that aging of the solutions resulted in a slight lowering of the velocity.

The measurements were then repeated, under the same conditions used in the first series of measurements, to ascertain the precision of the technique.

Third series	Time (in seconds)
Solution to be chromatographed	85
First extract	91
Second extract	78
Third extract	66
Filtrate	79

These results leave no uncertainty as to the constancy of the measurements.

A series of experiments was then carried out in which washing of the chromatograph was omitted.

Fourth series	Time (in seconds)
Solution to be chromatographed	85
First extract	88
Second extract	76
Third extract	63
Filtrate	41

These values show that both fractionation and purification can be accomplished by this technique.

The filtrate from the first series was chromatographed again, care being taken to wash the second chromatograph, as was done in the case of the first chromatograph.

Fifth series	Time (in seconds)
Solution to be chromatographed	79
First extract	90
Second extract	79
Third extract	66
Filtrate	68

These measurements are interesting in that they show the way in which the chromatograph of a filtrate with an initial low viscosity gives values almost identical with those of the original product. On the other hand, the next filtrate showed a lower viscosity on account of the accumulation in it of substances which tended to diminish the viscosity.

A final series was carried out under the same conditions as in the fifth series, except that the chromatograph was not washed and therefore that results comparable with those in the fourth series were obtained.

Sixth series	Time (in seconds)
Solution to be chromatographed	79
First extract	90
Second extract	78
Third extract	67
Filtrate	40

It was not possible to obtain chromatographs of the filtrates from the two series in which washing was omitted because they contained too little rubber. Hence they were of no particular interest anyway.

The question then arose as to why the filtrate of the chromatograph had a viscosity of the same order of magnitude as that of the second extract, in fact a slightly greater viscosity, whereas it would be expected to be lower than that of the third extract. The apparent exception in the fifth series is attributable merely to the fact that in this case the original solution was not used but rather the filtrate of a previous series, *viz.*, that of the first series. There is still less justification for comparing the fourth and sixth chromatographs, in both of which cases the washing operation was omitted.

It might be thought that there was an insufficient quantity of adsorbent for the solution to be chromatographed, but it is certain that products of low viscosity accumulate in the filtrate, as is evidenced by a comparison of the first and fifth series; in the filtrate a considerable quantity of a pseudo-phase accumulated, which differed, at least physically and perhaps also chemically, from the adsorbed rubber.

To study this phase, the quantity of which is small compared with that of the chromatographed total-rubber, it would be necessary to make chromatographs, not from the analytical point of view, as was done in the present work, but on a larger scale.

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THE PROPERTIES OF POLYMERS IN SOLUTION

X. ULTRAFILTRATIONS OF RUBBER SOLUTIONS *

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It is a recognized fact that ultrafiltration is one of the most valuable methods for the study and treatment of colloidal suspensions formed of compact spherical particles. Not only is it possible to separate this type of particle from a solvent by means of a suitable ultrafilter, but it is also possible to determine the size of the particles by means of calibrated ultrafilters[1].

Up to the present time, however, ultrafiltration has been utilized very little in the study of chain molecules, and no accurate data are available on the behavior of colloidal solutions of chain molecules during ultrafiltration. In the following discussion, the results of some experiments on the ultrafiltration of rubber solutions are described.

TABLE I

Type of filter [2] (Ultrafeinfilter)	Solution containing	Volume of solution (cc.)	Concentration (%)	Viscosity (η_{rel})	Pressure (atm. of CO_2)	Time (hours)	Filtrate	Rubber in filtrate (%)
"Finest" 150′	crepe	50	0.68	15	50	6	46	0
"Finest" 150′	latex	50	0.55	7.2	50	5	48	0
"Finest" 150′	crepe	50	0.116	1.7	50	5	48	0
"Fine" 100′	crepe	35	0.29	3.7	18	80	35	0
"Fine" 50′	crepe	35	0.29	3.7	18	40	35	0
"Rapid" 6′	crepe	35	0.29	3.7	18	30	35	0
"Rapid" 3′	crepe	35	0.29	3.7	10	45	35	0
"Rapid" 2′	crepe	35	0.28	3.7	10	60	35	0
"Rapid" 1′	crepe	35	0.29	3.7	5	60	35	0
"Rapid" 6′	crepe	75	0.028	1.11	10	45	75	0

Dilute solutions of rubber in toluene can be separated completely into rubber and solvent by ultrafiltration under pressure through fine ultrafilters with pores as fine as about 50 mμ (*"Fine" Cellafiltres* and *Membranfiltres*). Solutions of crepe and solutions of masticated rubber give the same results.

When a solution is filtered through an ultrafilter with pores of an average size of at least 50 mμ (*"Medium" Membranfiltre,* 10 seconds; *"Coarse,"* 3 seconds), a little rubber passes through, the quantity of which increases with the size of the pores, as would be expected (see Table I). However, only when the diameter of the pores of the ultrafilter is in the range of 0.5 to 3μ does any considerable quantity of rubber pass through at the beginning. Soon after this initial effect, the filters become almost impermeable, and only practically pure solvent then passes through.

On the other hand, when a fritted-glass filter with pores 5 to 30μ in size is used, the solutions pass through without leaving any residue.

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Evidently the long chains of rubber can pass freely only through very large pores; in the mass of cellulose micelles comprising the ultrafilter, which can be compared with a disordered heap of limbs and branches, the rubber fibers are caught firmly within this mass so that the pores in the latter finally become plugged up. Even treatment with solvent does not extract the rubber at all readily from the ultrafilter.

It is interesting to compare the length of the chains of rubber with the size size of the pores through which a minimum of rubber solution passes in the beginning. This diameter is approximately 0.5μ. If the molecular weight of crepe is assumed to be 200,000, which corresponds to about 300 isoprene residues 4 A.U. in length, the molecule has, when extended, a length of 4×3000 or 12,000 A.U., *i.e.*, 1.2μ.

It is difficult to believe that straight rods of this length can slip through the tortuous passages of an ultrafilter. However, it is improbable that the molecules are extended, and in the dissolved state and in the amorphous state the length is probably only a fraction of the maximum length. Stretched, crystallized rubber contracts during "fusion," *i.e.*, during its return to the amorphous state, to one-eighth of its original length. The isoprene chains, which are straight and lie parallel in the stretched sample, no longer show any regularity after their return to the amorphous state, and their behavior must be an image, on a molecular scale, of the behavior of the object which they constitute. The diameter of the unit which forms a chain, the length of which when extended is 12,000 A.U., becomes in the amorphous state about $\frac{1}{8} \times 12{,}000$ or 1500 A.U., *i.e.*, 0.15μ. One is therefore confronted with the fact that, for a mean increase in the length of the molecule of approximately 0.2μ, a socalled molecular suspension can probably pass through a filter with pores 0.5 to 1μ in diameter, yet can gradually stop up the filter.

The behavior of colloids having a chain structure is therefore different from that of compact colloids, and hence ultrafiltration can be utilized as a means of deciding, in doubtful cases, whether colloidal particles are in chain form or in the form of compact particles.

EXPERIMENTAL PART

Three materials were tested:

(1) Crepe rubber.
(2) Films obtained by pouring and drying preserved latex (Revertex).
(3) Masticated crepe.

One to two grams of rubber were treated with 150 cc. of toluene in an opaque flask for 3 hours, the flask being rotated slowly around an axis parallel to the bottom of the flask. The resulting solutions were poured through a fine-mesh screen, which retained the undissolved but swollen particles. The solutions were then centrifuged.

These solutions were clear, and when filtered through a fritted-glass filter their compositions remained unchanged. Hydroquinone was added to the solutions as a stabilizing agent. They were kept in darkness, and since their viscosities did not change during the course of the experiments, it was assumed that they underwent no degradation.

The concentrations of the solutions used for the experiments, as well as the concentrations of the ultrafiltrates, were determined by evaporation in a vacuum and subsequent weighing.

TABLE II

Type of filter	Size of	Solution of	Volume of solution (cc.)	Concentration (%)	Pressure (atm.)	Time (hrs.)	Filtrate (fraction and cc.)	Rubber (mg.)	Rubber in filtered fractions (%)	Total (%)
Membranfilter 220″	20-100 mμ	crepe	50	0.35	25	3	50	0	0	—
Membranfilter ("medium") 30″	0.1-1μ	crepe	50	0.35	7	2	(1) 25	1.2	1.6	
							(2) 24	0	0	0.8
Membranfilter ("coarse") 10″	0.5-3μ	crepe	50	0.35	5-12	2	(1) 22	2.7	4	
							(2) 28	0.3	0.35	2
The filtrate was digested in 50 cc. of toluene	—	—	—	—	12	2	(1) 22	0.2	0.3	
							(2) 28	0.2	0.23	0.26
Membranfilter ("coarse") 3″	0.5-3μ	crepe	50	0.35	5-10	2	(1) 26	11.5	14.5	
							(2) 24	0.5	0.7	7.9
The filtrate was digested in 50 cc. of toluene	—	—	—	—	15	2	(1) 25	0.6	0.79	
							(2) 25	0.5	0.66	0.72
Membranfilter ("coarse") 1″	0.5-3μ	crepe	35	0.35	5-15	1	(1) 8	21.	82	
							(2) 7	10.7	50	—
							(3) 8	0.9	3.6	
							(4) 10	0.2	0.2	31.8
The filtrate was digested with 35 cc. of toluene	—	—	—	—	15	1.5	(1) 18	0.3	0.55	
							(2) 16	0.2	0.42	0.48
Membranfilter ("fine") 35″	1 to 50 mμ	crepe	50	0.59	5-10	2	(1) 18	1.3	2	
							(2) 32	0.7	0.6	1.1
The filtrate was digested with 50 cc. of toluene	—	—	—	—	10	3	—	0	0	0

The ultrafilters, the effective diameter of which was 6 cm., were obtained from the Physikalischen Werkstätten A.-G. of Göttingen. The numerical designations of the filters refer to the number of seconds (minutes for the *Ultrafeinfilters*) required for 100 cc. of distilled water to pass through under a vacuum set up by a water pump, with a filter surface of 80 sq. cm. An apparatus was obtained from the same company for carrying out the filtrations. This apparatus was equipped with a magnetic device which made it possible to keep the liquid agitated during filtration. Table I gives the results of a series of experiments.

In each case after filtering, 50 cc. of toluene was poured on the filter in the filtration apparatus and was agitated for 5-6 hours, after which time the toluene was filtered under pressure. In this first series of experiments only pure toluene passed through the filter.

A second series of experiments was then carried out with nitrocellulose filters (*Membranfilter*). In this case it was necessary first of all to allow the moist filters to stand in propyl alcohol to remove water (ethyl alcohol destroys this particular type of filter), then in toluene.

In this second series of experiments the filtrates were separated into fractions, the rubber contents of which are shown in Table II. The data show that the filters became plugged up during the filtrations.

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[1] See, for example, Elford, *Trans. Faraday Soc.* **33**, 1094 (1937).
[2] The socalled "rapid" ultrafilters retain fine particles of gold; the "medium" ultrafilters retain benzopurpurine; the "fine" ultrafilters, for dialysis and osmosis, retain albumins with high molecular weights; the "finest" ultrafilters retain Congo red and albumin. See Zsigmondy, *Z. physik. Chem.* **111**, 211 (1924).

ON THE CRYSTALLIZATION OF CRUDE RUBBER *

CHULLCHAI PARK

I. EXPERIMENTAL RESULTS

CRYSTALLIZATION BY VARIOUS METHODS

It has already been ascertained that crystallization of rubber can be induced in various ways, such as stretching, freezing, milling and compressing.

If a narrow strip of smoked sheet rubber is stretched extensively, the x-ray diffraction pattern shows a fibrous arrangement of the microcrystals. At an elongation of about 150 per cent, a faint fibre diagram is obtained and at 500 per cent elongation, the diffraction spots become sharp and intense. The amorphous halo peculiar to unstretched rubber remains unchanged in width and position, but its intensity decreases with increase in elongation, in contrast to the increase in intensity of the fibrous spots.

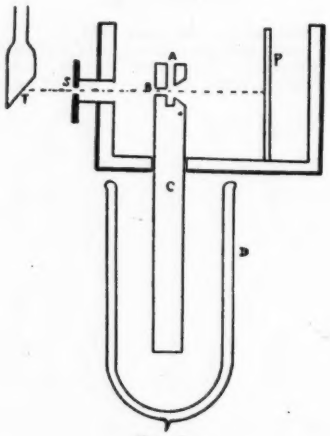

FIG. 1.

It was found by Katz and Bing[1] that crepe rubber is crystalline. This point was confirmed by Tanaka and the writer; the Debye-Scherrer rings obtained by them with crepe rubber is shown in Fig. 1 of Plate I. In preparing a sheet of crepe rubber, coagulated strips are passed between rolls 8 to 12 times, and the coagulated strips are strongly crystalized by such severe milling. In preparing smoked sheet, milling of the coagulated sheets is not so severe as in the case of crepe rubber, and some of the rubber crystals formed during milling melt when heated in the process of smoking.

To take a photograph of frozen rubber, the specimen must be kept frozen throughout the exposure. For this purpose use was made of the simple apparatus shown in Fig. 1, which was devised by Yoshida and Tsuboi[2]. In this diagram

* Reprinted from the *Memoirs of the College of Science, Kyoto Imperial University*, Series A, Vol. 22, No. 1, pages 13-25, January 1939.

C is a copper rod, and the specimen to be examined is inserted in a small vertical hole A in the upper part of the rod C. The small horizontal hole B passing through the upper part of the rod C is a slit for the x-rays. The x-rays, starting from a Cu or Fe target of a Shearer tube, illuminate the specimen in hole A, after passing through the slits S and B; and the pattern of the diffracted x-rays is impressed on the photographic plate P perpendicular to the incident x-ray beam. The specimen of rubber is kept frozen by immersion of the lower part of the copper rod C in a suitable freezing mixture. Acetone and dry ice was used as a freezing mixture and the temperature of the frozen specimen was determined by inserting a thermometer into hole A. Smoked sheet was used in this case. At $-5°$C, the powder diagram shown in Fig. 2 of Plate I was obtained; but at 0° C no interference fringe was detected. This means that smoked rubber does not crystallize at about 0° C, unless it is kept for a long time at that temperature. However when it is kept cooled at 0° C for a long time, *e.g.*, two weeks, crystallization is appreciable.

A piece of smoked sheet, $2\times4\times0.2$ cm., was put between two bronze plates, $7\times7\times0.3$ cm., and pressed at 5-6° C for about two weeks by putting a weight of 3.5 kg. on the upper plate. The specimen was found to be crystallized, as appears in the powder diagram shown in Fig. 3 of Plate I.

Very recently, Thiessen and Kirsch[3] reported an interesting experiment on the crystallization of rubber by compressing. In general rubber crystallizes at a higher temperature when the degree and duration of compressing are increased.

When a strip of rubber kept slightly stretched in an uncrystallized state is frozen, it gives an imperfect fibre diagram, consisting of short arcs, as shown in Fig. 4 of Plate I. The fibre axis lies in the direction of stretching. Furthermore when a sample of rubber inserted in hole A of Figure 1 is frozen by being slightly pressed by placing a thermometer on it, it also gives a fibre diagram, consisting of short arcs as shown in Fig. 5 of Plate I. In this case the fibre axis is perpendicular to the direction of pressing.

When a sufficiently stretched strip of rubber is released and its contracted length becomes 1.7 times the original length, it shows no crystalline interference at room temperature. But when it is frozen at a temperature lower than about $-5°$ C it gives an imperfect fibre diagram, as shown in Fig. 6 of Plate I. The fibre axis is in the direction of stretching. These facts indicate that when rubber is stretched or compressed a little at room temperature it approaches the crystalline state, though it is not yet perfectly crystalline, and that this tendency to crystallize is completed by subsequent freezing.

Contraction when Tension is Released

The remarkable contraction which takes place when tension is released is one of the characteristic properties of rubber. When the tension is released immediately after stretching at room temperature, crude rubber contracts almost, though not quite, to its original length. When, however, the tension is released after many hours of continuous stretching, the contraction is far less. The contraction of a strip of smoked sheet in relation to the time of continuous stretching at about 20° C is shown in Fig. 2.

One cm. of a strip of smoked sheet was stretched 5-fold or 8-fold and after being stretched for a certain time the tension was released and the length measured immediately. The difference of the lengths in the stretched and released state was taken as the amount of contraction, as shown in Fig. 2.

PLATE I

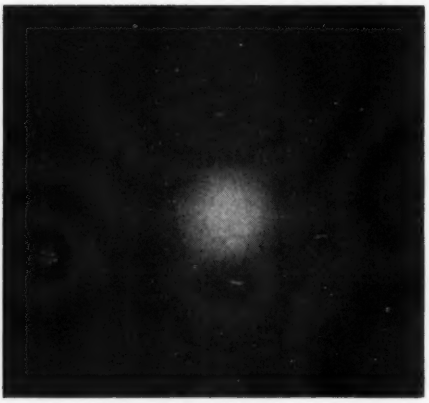

FIG. 1.

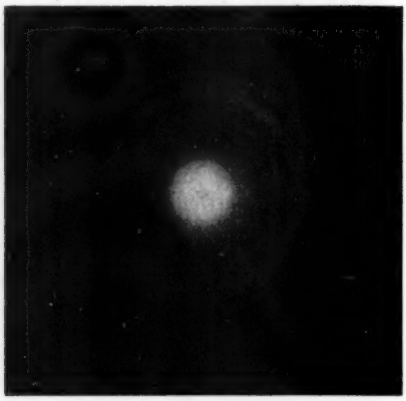

FIG. 2.

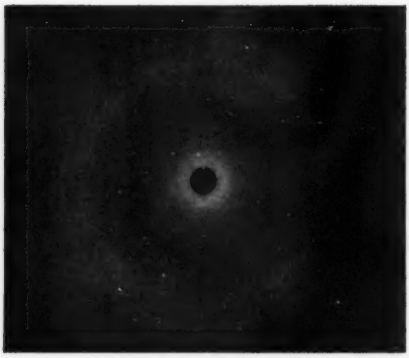

FIG. 3.

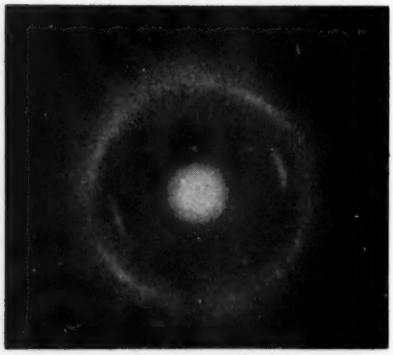

FIG. 4.

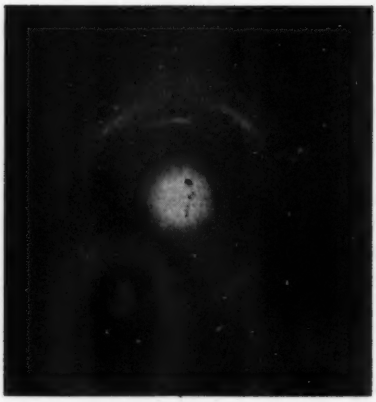

FIG. 5.

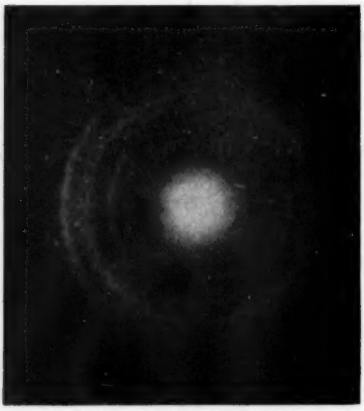

FIG. 6.

Next the slow change of contraction of a strip of smoked sheet after release of tension which had been applied for a certain duration of time was measured. The results obtained at about 20° C are shown in Fig. 3. In this case all specimens were stretched 5-fold, and the lengths of the specimens, which are represented as ordinates, refer to 1 cm. of the original length before stretching. As is seen in Fig. 3, the greater part of the contraction occurred at the moment

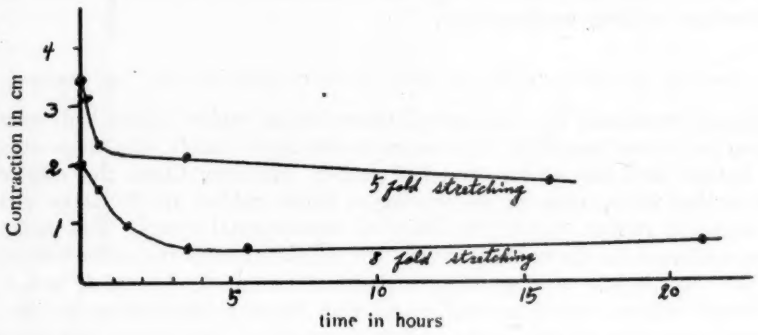

FIG. 2.

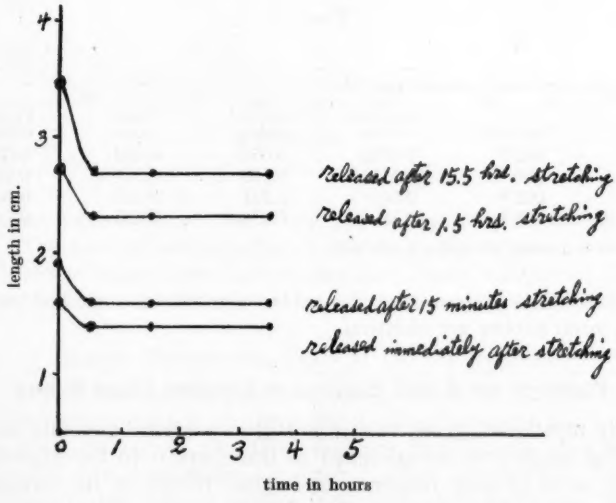

FIG. 3.

when the tension was released, and the remaining contraction was complete within the following 30 minutes. In general the speed of contraction of stretched crude rubber after the release of the tension increases with increase in temperature. Contraction proceeds very slowly at low temperatures but rapidly at elevated temperatures.

Strongly stretched rubber shows a fibre diagram with sharp spots. When contraction after release of the tension is small, the sharp spots of the fibre diagram become somewhat diffuse and they extend to form circular arcs. This

fact indicates that the parallelism of the crystallites along the fibre axis is partially destroyed by release of the tension, although the fibrous arrangement is still roughly maintained.

When such slightly contracted crude rubber is warmed gently, it contracts very slowly, and when it has become about twice its original length before stretching, the arcs of the fibre diagram extend gradually into broad circles, and at last they are displaced by the diffuse amorphous halo peculiar to the unstretched original crude rubber.

Identity of the Crystals Obtained by Stretching, Milling and Freezing

Barnes[4] examined two samples of frozen crude rubber which had remained frozen for a very long time. His measurements agree closely with those obtained by Lotmar and Meyer[5] for stretched rubber. Recently Clark and others[6] reported that the spacings of the crystals in frozen rubber are the same as those in stretched rubber, within the limits of experimental errors. This point has been confirmed by the present writer. He calculated from the diffraction photographs the spacings corresponding to four intense spots, A_1, A_2, I_1 and I_2 for stretched rubber, and compared them with those corresponding to the four intense rings due to pale crepe and frozen rubber. The results are shown in Table I.

Table I

		$\sin\theta/\lambda$			
		Lotmar and Meyer	Park		
Spot	face hkl	Stretched rubber	Stretched rubber	Pale crepe	Frozen rubber
A_1	002 *	0.0795	0.080	0.081	0.081
A_2	200 *	0.118	0.120	0.118	0.122
I_1	012 *	0.100	0.101	0.100	0.103
I_2	013 *	0.133	0.134	0.131	0.136

* Indices refer to Lotmar and Meyer's unit cell.

The data in Table I show that the rubber crystals in stretched rubber, pale crepe and frozen rubber are identical.

Fusion of the Rubber Crystals in Stretched Crude Rubber

As already mentioned, crude rubber is still in a crystalline state after release of the tension applied to the specimen to transform it to the crystalline state. The melting point of such rubber crystals after release of the tension depends on the elongation and on the time elapsed after release of the tension. But, as is revealed by the contraction experiment shown in Fig. 2, the melting point seems to reach nearly its maximum value within about three hours after release of the tension. The writer measured, after one day from release of the tension, the melting points of smoked sheet which had been stretched to various different degrees. The results are tabulated in Table II.

Table II

Stretching degree	3.2-fold	4.0	5.1	5.6	6.4	7.2
Melting temperature	25° C	26	26	27	27	30

As is evident from the table, the melting point increases gradually with increase in the degree of stretching.

Next the melting point of smoked sheet in the stretched state was measured by x-ray diffraction. The melting point in this case has a different meaning and is generally much higher than before. The relation between the melting point and elongation is shown in Fig. 4.

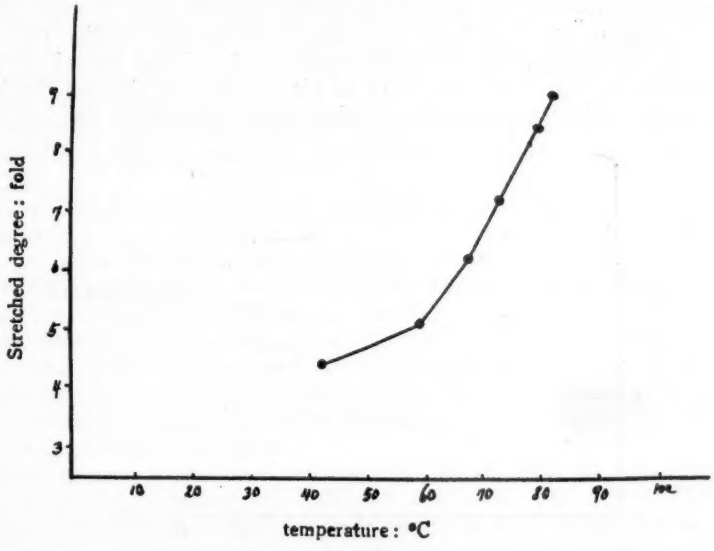

FIG. 4.

The melting point of the rubber crystals of frozen smoked sheet is about $10° \pm 1°$ C. The melting point of crystals in smoked sheet which has been worked and then frozen is higher than that of unworked frozen rubber; in this case the melting temperature increases with increase in the degree of working.

SLIPPING BETWEEN THE CHAIN MOLECULES OF RUBBER

When a strip of smoked sheet is stretched to about 7-8 fold its initial length and is simultaneously heated at about 80° C for about one hour, it gives an amorphous halo instead of the fibre diagram peculiar to stretched rubber. To explain this, two suggestions are offered. The first assumes that thermal agitation separates the chain molecules from each other and from their position in the crystal lattice. The second accepts this theory and adds the idea that the molecules, slipping on one another, coil up to their original position, restoring the stretched rubber to its original unstretched state.

No crystalline photograph is obtained in either case, but the contraction, when the tension is entirely released after heating, is different in the two cases. If the first theory is correct, the contraction which takes place when tension is entirely released after heating is of the same order as that when the tension is entirely released without heating in the stretched state. On the other hand if the second explanation is correct, the contraction is much smaller than that when the tension is released without heating in the stretched state.

When a narrow strip of smoked sheet is stretched, without heating, to about 7-8 fold its original length for about one hour, and is immersed in boiling water for about ten minutes after release of the tension, its length shortens to about 1.2 times its initial unstretched length, which may be considered as almost the same as the initial length. But when the same specimen, after being stretched to the same amount for about one hour, is heated to its melting point, *i.e.*, 70° C or 80° C in the stretched state, and is immersed in boiling water for about ten minutes after release of the tension, its length shortens only to about one-half of the elongation, *i.e.*, 3 or 4 times its initial unstretched length. The results of such an experiment with a ribbon stretched 7.4-fold and heated at various temperatures are shown by the curve in Fig. 5. In this diagram the lengths of the rubber strip when heated in boiling water, referred to one cm. of the

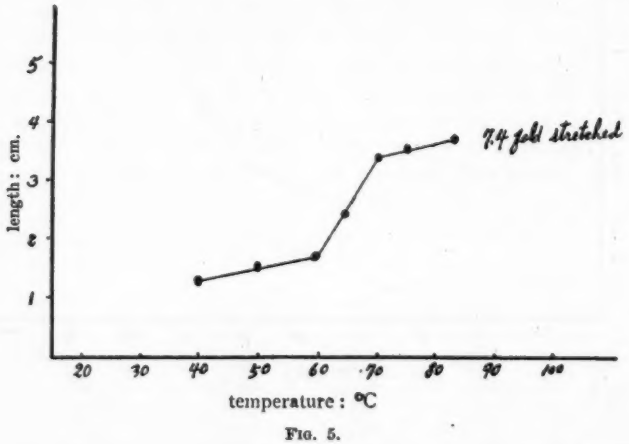

FIG. 5.

initial length, are plotted as ordinates, the temperatures during stretching as abscissas. This curve shows that heating a piece of rubber above its melting temperature while stretched causes to a remarkable degree, though not perfectly, a coiling and mutual slipping of the spiral molecules.

II. A THEORY OF CRYSTALLIZATION OF RUBBER

Unstretched rubber gives an amorphous ring and stretched rubber gives a fibre diagram, and various theories have been proposed to explain these facts. Katz[7] believes that the isoprene complex of rubber is chain-like in both states. Stretching merely brings the straight chains into alignment. This theory does not explain adequately the remarkable extensibility of rubber. In the discussions already referred to[8,9], Astbury shows that the maximum possible extensibility of rubber with such straight-chain molecules is only about 57 per cent, and it is not possible to explain the enormous extensibility of rubber, which amounts to several hundred per cent.

Kikentscher and Mark[10] and others consider that unstretched rubber is composed of isoprene spirals. Two isoprenes make one turn of the spirals, and stretching straightens the spirals into the chains of von Susich's model. This theory explains adequately the remarkable extensibility of rubber.

Hauser[11] reported that he had isolated two components of rubber, "sol rubber" or "alpha rubber" and "gel rubber" or "beta rubber," and by means of these terms attempted to explain the cause of the appearance of the interference spots when rubber is stretched. This theory likewise does not seem to explain the remarkable extensibility of rubber.

In 1934, Mack[12] proposed an interesting theory of the elasticity of rubber. According to him there appear to be only two possible and at the same time reasonable sources of force required to pull extended rubber molecules back to the unstretched position when the tension is released: (1) residual valences of the double bonds and (2) van der Waals forces between hydrogen atoms on the surface of the molecules. Between the two, Mack considers that the available evidence favors the latter.

In the same paper, Mack proposed a zigzag model of rubber molecules, and succeeded to a considerable extent in explaining the extensibility and contraction of rubber.

Meyer[13] tried to explain the crystallization of crude rubber on stretching by assuming long chain molecules; and at the same time explained the contraction when tension is released by thermal agitation of long-chain molecules.

In 1936, a schematic representation of the long-chain molecule in unstretched rubber was proposed by Simard and Warren[14].

Very recently Kuhn[15] proposed a "Knäuel" model of long-chain molecules in an elastic solid substance, and tried to explain elasticity and crystallization by assuming the possibility of free micro-Brownian movement of every small part of a long-chain molecule and the impossibility of the macro-Brownian movement of the molecule as a whole.

All the theories cited above are concerned chiefly with the crystallization of crude rubber by stretching and milling, but crystallization of crude rubber to the same lattice form by freezing or compressing must be taken into account equally. It is therefore necessary to consider another molecular configuration of crude rubber in the unstretched state. Let us imagine, as shown in Fig. 6, that a long chain molecule forms a large irregular spiral which contains numerous isoprenes in one turn, and that the long-chain molecules are in thermal agitation, corresponding to their temperature.

Fig. 6 represents schematically the configuration of an irregular spiral of a single long-chain molecule. Actually a long-chain molecule may be in the form of an irregular spiral in some parts, but in another part, it need not be so, on account of becoming entangled with other spiral groups of long chain molecules; consequently by assembly of the spiral groups, it may lie in a higgledy-piggledy manner, as shown in Fig. 7.

When a piece of rubber is stretched, the large irregular spirals of long-chain molecules straighten along the direction of elongation, and the straightened chain molecules fit together to form the crystal lattice by van der Waals force of attraction between the chain molecules. Of course it may be possible that a large irregular spiral contains straight chains in some parts. If so, such short straight chains may form a smaller crystal lattice by uniting with those in the neighboring large irregular spirals before the large irregular spirals are straightened by stretching.

Next, when a piece of rubber is frozen or hydrostatically compressed, neighboring chains of large irregular spirals attract each other and unite to form the crystal lattice by straightening.

Now let ribbons of smoked rubber be stretched to various degrees up to 800 per cent in the manner shown in Fig. 8 *a*, and then be cooled in the stretched

state at a temperature lower than about 0° C for two or three days; in this case on cooling a small elongation, *i.e.*, about 2-4%, occurs, as shown by the curve in Fig. 8 *b*. A strip of smoked rubber was stretched and its ends fastened

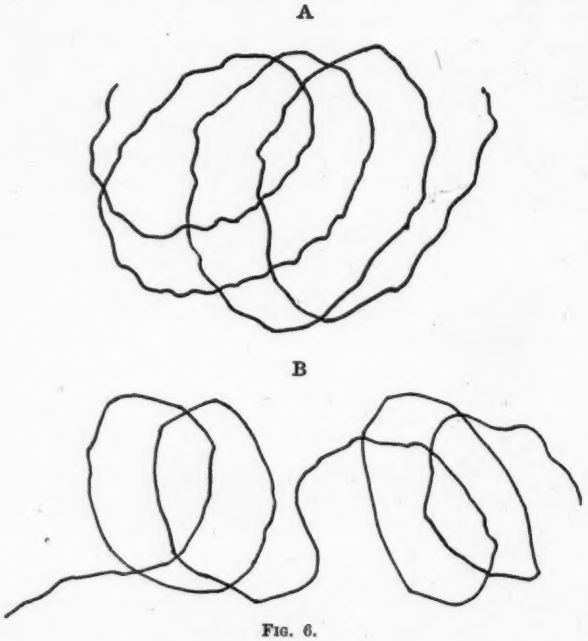

FIG. 6.

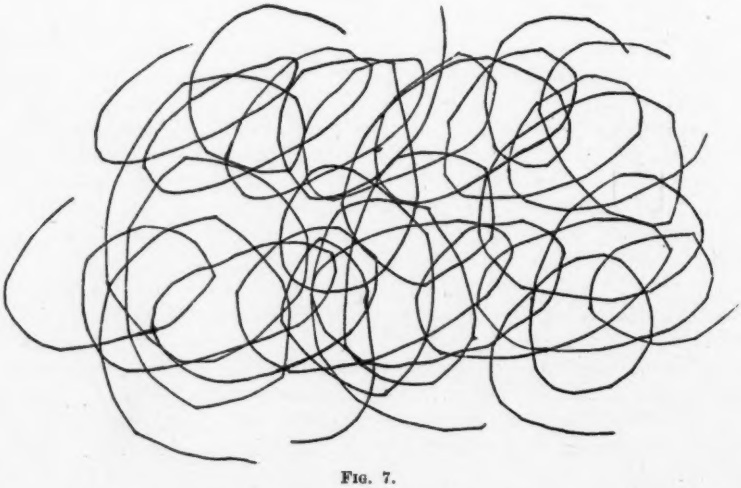

FIG. 7.

to the metal frame, as shown in Fig. 8 *a*, making its length 10 cm., and then it was cooled below 0° C while stretched. On cooling, a small residual elongation of the order mentioned above was found when the elongation was below about 600 per cent, and this was a maximum when the elongation was about

200-300 per cent. This fact seems to be in accordance with the view that the chains in the large irregular spirals straighten themselves in forming the crystal lattice by freezing. When the elongation exceeds about 600 per cent, the elongation on cooling, as stated above, is scarcely discernible.

This seems to be due to the fact that straightening of the chains of the large irregular spirals in the direction of stretching is already almost complete under such severe conditions of stretching, and that no more straightening of the chains occurs on cooling.

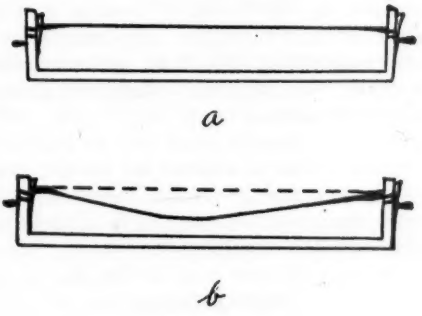

FIG. 8.

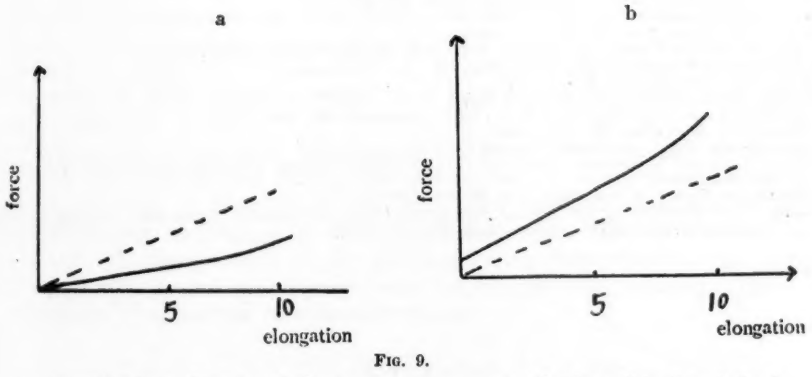

FIG. 9.

- - - contractive force along the spiral axis
—— attractive force between the neighbouring chains side by side

- - - contractive force along the spiral axis
—— attractive force between the neighbouring chains side by side

In order to understand the crystallization of rubber, it is helpful to compare the contractive force along the axis of the large irregular spirals with the attractive force side by side between the neighboring chains of the spirals. This comparison is shown schematically in Fig. 9. As stated before, the crystallization of rubber is due to the attractive force between the neighboring chains side by side, which may be termed a crystallizing force. Above room temperature, the crystallizing force is suppressed by the contractive force along the spiral axis, as shown by Fig. 9 a. However, when rubber is stretched sufficiently, the latter force is balanced by the external force applied in the stretching by setting free the former force to cause the crystallization. At a lower temperature, *i.e.*, below about 0° C, the attractive force between the neighboring chains side by

side, *i.e.*, the crystallizing force, becomes predominant and greater than the contractive force along the spiral axis by the decrease in thermal agitation, as shown by Fig. 9 b, irrespective of the degree of stretching; and crystallization occurs without any stretching.

When the tension of stretching is released at a temperature higher than room temperature, the contractive force along the spiral axis is set free, and is stronger than the crystallizing force at that temperature; curling of the chains into the original large irregular spirals disjoins the crystalline configuration and makes the stretched specimen contract as a whole.

When rubber crystallized by stretching or freezing is stored for a long time, the melting point of its crystals increases. This seems to be due to the fact that the chain molecules of rubber fall more perfectly and more tightly into the crystal lattice by aging, thus making it more and more difficult to disjoint it to the original amorphous state.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to K. Tanaka and S. Shimadzu for the facilities afforded during the experiments.

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BEHAVIOR OF RUBBER HYDROCARBON IN A MOLECULAR STILL *

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INTRODUCTION

Some investigators believe that rubber consists of associated molecules, and others accept Staudinger's view that long-chain molecules are formed by polymerization. Pummerer, Andriessen and Gündel[1] have obtained a molecular weight as low as 600. Meyer and Mark[2] believe that it is approximately 5,000, although they calculated on the basis of osmotic pressures values as high as 350,000.

They, as well as Pummerer, consider that rubber is an associated colloid and that high molecular weights are caused by aggregates, sometimes called micelles. Staudinger[3], however, considers that the long-chain rubber molecule itself has a molecular weight of 200,000 or even 350,000, and that products with lower values, which may be formed in rubber, result from degradation.

If the molecules are small it might be possible to distil them if their vapor pressure could be sufficiently increased, but none would distil without decomposition if the molecules are very large. Because the vapor pressure of rubber below its decomposition temperature is low, it appeared of interest to attempt to distil the material in a molecular still. Paraffin wax and sugar, both substances of relatively high molecular weight, have been successfully distilled in this type of apparatus[4].

Subsequent to the work described in this paper, the molecular weight of sol rubber prepared at this Bureau was determined by Kraemer and Lansing[5] of E. I. du Pont de Nemours & Co., Inc. They used the Svedberg method of sedimentation equilibrium in an ultracentrifuge with ethereal solutions of sol rubber. The temperature of the solutions during determinations was approximately 10° C, and an average value of 460,000 was obtained. There was evidenced of a mixture of molecular species.

APPARATUS

The stills, used in the attempt to distil rubber, consisted essentially of Pyrex Dewar flasks to which side-tubes were sealed that connected the flask to a mercury pump and its auxiliary equipment. The distance between the distilling and condensing glass surfaces was about 7 mm., and the area of the distilling surface was approximately 60 sq. cm. The still was connected to a pumping system, equipped with a suitable trap to condense mercury vapor, and the apparatus was thoroughly evacuated before a distillation was attempted. When distillation extended over many weeks continuously, an automatic control was necessary, and between the still and the trap there was a device to isolate the high-vacuum system when the mercury pump or its condenser ceased to function. When either event occurred, a column of mercury automatically rose, effectively

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 22, pages 529-533, May 1939.

sealed the still, and maintained the low pressure within it. Simultaneously, a bell began to ring as a warning of trouble.

The equipment is illustrated in Figures 1 to 4. The mercury cutoff is shown in Figure 1. The length of the tube must be properly adjusted so that the mercury in *B* will rise to close the inner tube in *C* when it responds to atmospheric pressure. In Figure 2, tube *B* is an extension of its union with the mercury well of the cutoff. A Pyrex rod was welded to the stopper of stopcock *C*. In the closed position, the stopper was supported by a string over the pins, as shown in the diagram. The string ended in a loop which was held at *D* by the catch at *C*. The catch, which resembles that on a common type of mousetrap,

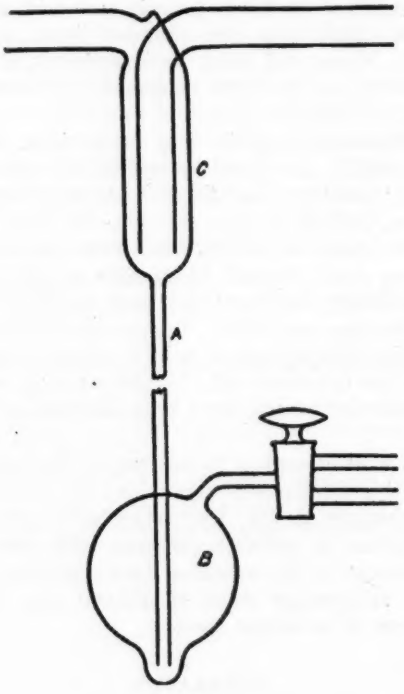

FIG. 1.

was opened when a current flowed through the electromagnet. The latter was operated by dry cells. When the catch was opened, the string was free to move, and was drawn away by a 200-g weight. The capillary shown at *A* in Figure 2 prevented any surging of the mercury. At *E* are shown the contact points of a relay which closed when the heater current to the pump was interrupted.

Figure 3 is a diagram of a switch, operated by water flowing to the condenser. The circuit to the electric heater of the pump was completed through tungsten contacts and mercury. The pressure of water passing through the tube, *AB*, to the condenser of the pump caused the mercury to rise and make contact. Two screw clamps at *A* and *B* regulated the speed and the head of the flow of water. In operation, the pressure head was so adjusted that the mercury stood well above the upper contact with water flowing, and well below when the flow

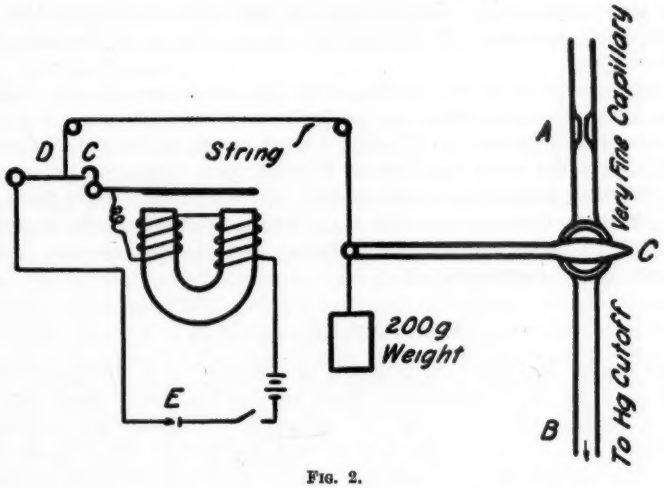

FIG. 2.

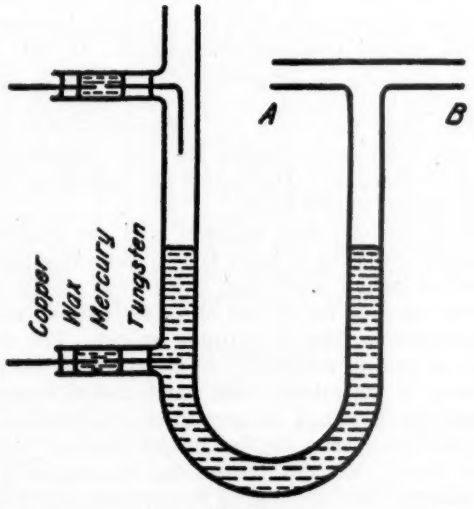

FIG. 3.

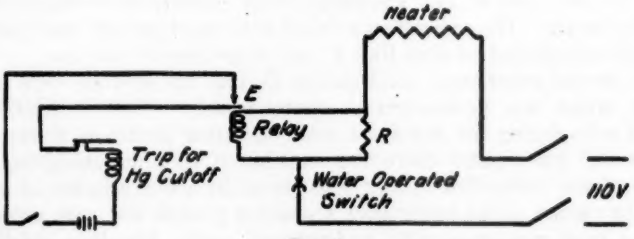

FIG. 4.

of water stopped entirely. The position of the upper surface of the mercury was so adjusted that small fluctuations of the waterhead in the mains did not open the contact.

A wiring diagram is shown in Figure 4. The resistance, R, was sufficient to keep the relay, E, open when the heater current was flowing. For a heater drawing about 2 amperes at 110 volts, 5 or 6 inches of No. 26 Nichrome wire was used. Since the relay contacts at E were open when current was flowing through the relay magnet, any interruption of the current caused them to close, and completed the circuit to the trip of the mercury cutoff. If the heater current was stopped, the relay current also stopped, and in this case also the trip of the mercury cutoff responded.

EXPERIMENTAL RESULTS

Pure sol rubber hydrocarbon, prepared as described in a previous publication[6], was used in all of the experiments. Since the sol fraction is more mobile than the gel, it seemed probable that its molecules would become detached with greater ease. A solution of the rubber hydrocarbon in ether, saturated with nitrogen, was introduced and carefully spread over the distilling surface. The ether was removed at low pressure. The pressure maintained during distillation was too low to be measured by a McLeod gage, since the so-called "click" vacuum was obtained. Experiments with temperatures between 100° and 150° C around the distilling surface produced no distillate. At 160°, after a few days, a faint deposit was observed on the condenser by using a suitable lens, and in subsequent experiments this temperature was maintained by a heating coil.

Three distillations were performed for different periods and with different temperatures in the condenser. During the first experiment the condensing surface was chilled by liquid air. Distillation was conducted each day for about 8 hours for a total period of 100 hours.

The outer wall of the still was removed, and the condensing surface was washed with acetone. By using a hand lens, a very thin layer of transparent material, estimated to be not more than 2 mg., was visible on the condensing surface. A little was removed on the end of a glass rod and momentarily heated. There was a characteristic odor of burning rubber. The deposit was feebly extensible but did not recover completely when deformed. Its physical properties were more like those of the rubber from which it had been distilled than the properties of distillates obtained in any later experiments. Rubber of low molecular weight may have been distilled in this instance.

An earlier note[7] stated that this Bureau had succeeded in distilling purified rubber without decomposition by heating it in a high vacuum to the temperature of boiling water. This statement was based on the results of this experiment. However, the temperature of distillation was not that of boiling water, but 160° C. On the basis of this statement, Lens[8] attempted a similar distillation with crude rubber. His experiments failed entirely, however, and probably the temperature of distillation was 100° C and consequently too low.

For the second experiment, solid carbon dioxide and acetone were used in the condenser, which was maintained at approximately −78° C. Distillation was conducted only during the day for a total operating period of about 250 hours. When the still was opened there was an odor of levulinic aldehyde, and when a portion of the undistilled rubber was placed in a hot solution of ammonium acetate, the vapors of the latter gave a positive pyrrole test with a pine shaving which had been moistened with hydrochloric acid[9]. Levulinic aldehyde is an

oxidation product of rubber that responds to the pyrrole test. The thin layer of distillate was transparent, hard and insoluble in carbon disulfide. There was about 5 mg. of distillate.

A third experiment was conducted with tap water in the condenser. The distillation was continuous over 140 days, and during most of the period the temperature of the tap water varied from 8° to 10° C. At the end of the experiment, the residue of undistilled rubber was clear, almost colorless, and recovered slowly when deformed. The material deposited on the condenser, amounting to not more than 20 mg., was visible without a lens. It had collected in droplets, was transparent, hard and not extensible or plastic. There was a marked odor of levulinic aldehyde in the distillate and in the undistilled residue. The distillate was insoluble in ether, benzene, chloroform, ethyl acetate, alcohol and acetone. Enough of it was scraped from the condenser for a determination of its iodine number by the Kemp-Wijs method[10], but with a dilute solution of iodine. Although the material was insoluble in carbon disulfide, it swelled sufficiently to permit penetration by the iodine solution. The end point was definite. A value of 328 was obtained. The iodine number of purified rubber, determined by the same procedure, was 370. The degree of unsaturation of a cyclic rubber, which was made by incorporating sulfonic acids and heating to 140° C, has been reported as 55 to 65 per cent of that of the rubber hydrocarbon[11].

Marked oxidation had undoubtedly occurred during the second and third experiments. The original ethereal solution, though saturated with nitrogen before it was introduced into the still, was exposed to air during the process. It was hoped that any oxygen dissolved in the rubber as a result of this exposure would be removed at the low pressure used, but apparently some was retained. Furthermore, cyclic rubber may have slowly formed at 160° C, and may have distilled. In the second and third experiments, the marked difference in the physical characteristics of the distillate which had been maintained at 10° C, and that of the undistilled rubber which had been heated to 160° C, suggests this possibility. Rubber has a marked tendency to form cyclic compounds, and Kirchhof has shown that they are produced at 200° C.

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SPECIFIC HEAT OF STRAINED RUBBER *

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The specific heat of unstrained rubber as a function of temperature has been the subject of many investigations; but only one set of data has been published on the specific heat of strained rubber. (Ornstein, Wouda and Eymers, *Proc. Acad. Sci. Amsterdam*, **33**, 273 1930). Ornstein and his coworkers heated samples of strained vulcanized rubber to 80° C and dropped them into a calorimeter at room temperature. The results they obtained are presented in Figure 1, where the specific heat of one gram of rubber is plotted against extension:

$$\Delta l = \frac{l - l_0}{l_0}$$

where l = length of strained sample
l_0 = length of same sample unstrained

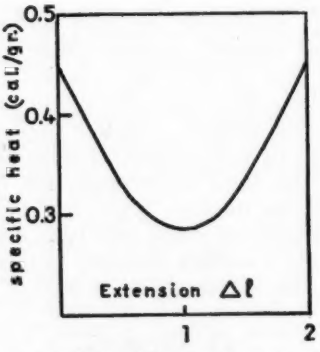

FIG. 1.—Specific heat of strained rubber, after Ornstein, Wouda, and Eymers.

As Figure 1 shows, the specific heat diminishes to about two-thirds of its original value when the extension is increased from 0 to 100 per cent ($\Delta l = 1$); it increases again on further extension. According to Ornstein *et al.*, "the form of the curve for the specific heat is most interesting, as the strong variation of this quantity with the elongation must be of utmost importance for the understanding of the molecular state of rubber."

In order to check these results by another method, the writer measured the specific heat of rubber at room temperature (19° to 21° C) by a process involving temperature changes of less than 0.1° C. Two samples of rubber were chosen. Sample I was highly vulcanized for 30 minutes under 3 atmospheres' pressure. Its composition was as follows:

Smoked sheet	89
Sulfur	1.8
Accelerator	0.9
ZnO, carbon black	8.3

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 31, No. 6, pages 761-762, June 1939.

Sample II was a patented, pure crepe, milled, pressed, calendered rubber; it was unvulcanized and contained no fillers. A band-shaped piece of rubber was cut from each sample, the same piece was studied at several extensions.

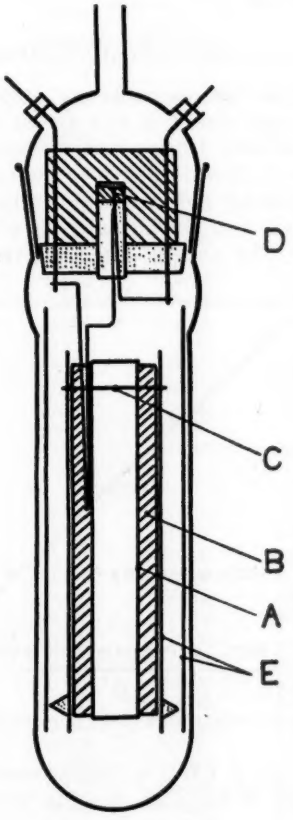

FIG. 2.—Calorimeter.

CALORIMETER

The heating unit (Figure 2) is made of constantan wire, 0.2 mm. in diameter, with a resistance of 7.6 ohms; it is coiled around the thin-walled copper tube, *A* (10 mm. in diameter, 75 mm. long, 0.1 mm. thick) and insulated with Bakelite. One end of the band-shaped rubber, *B*, is held by a steel pin, *C*, soldered transversely through the copper tube. The rubber is then wound over the heating unit under a constant strain produced by a weight attached to the free end. The latter is finally attached also to the same pin. One of the copper-constantan junctions of the thermocouple (constantan 0.2 mm., copper 0.15 mm.) is thus placed between the heating unit and the rubber band; the other junction, *D*, is forced into a hole in the center of a 70-gram copper block. The calorimeter is placed in a glass container with a ground joint and can be evacuated. The rubber and the internal face of the glass container are recovered by light alumi-

num foils, *E*, which reduce the losses by radiation. The whole apparatus is immersed in a Dewar flask.

The thermocouple is connected to a Kipp and Zonen galvanometer, type Zc. The heating coil and its connections (which serve also to suspend the heating unit) are not shown in Figure 2.

CALIBRATION AND MEASUREMENTS

The two junctions of the thermocouple are attached to the bulbs of two Beckmann thermometers and placed in two Dewar flasks filled with water of slightly different temperatures. During temperature equalization, readings of the arbitrary temperatures indicated by the two thermometers and of the position of the spot on the galvanometer scale are made every 2 minutes. The difference between the readings of the two thermometers is plotted against those of the galvanometer (Figure 3). The slope of the curve thus obtained gives the cali-

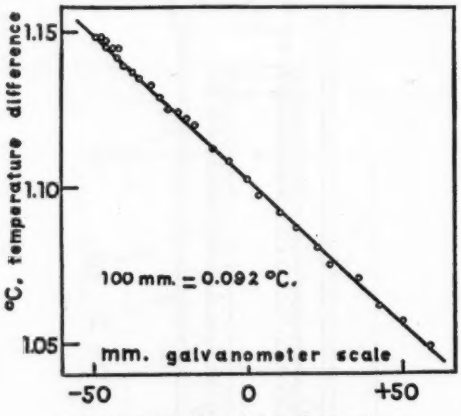

FIG. 3.—Calibration of the galvanometer.

bration. In the present case a 100-mm. displacement of the spot corresponds to a temperature difference of 0.092° C, with an accuracy better than one per cent.

One hour after the rubber band is mounted, readings of the galvanometer are made at intervals of 30 seconds over a period of several minutes. A current of known intensity (between 0.08 and 0.18 ampere) is sent through the heating coil for 5 to 30 seconds, and the readings are continued for 5 minutes. (It was found that a regular slope of the time-deflection curve is practically attained after 2 minutes.) The increase of temperature corresponding to a known energy input, and thus the total heat capacity of the rubber and the heating unit, can be easily deduced. The heat capacity of the heating unit, calculated from its components (copper, constantan, aluminum, Bakelite), was found to be 0.97 calorie per ° C, about 20 per cent of the heat capacity of the rubber band. By deducting 0.97 from the total heat capacity and dividing by the weight of the rubber, we obtain the specific heat of the rubber.

RESULTS

The experimental data are given in Table I and summarized in Figure 4, where the values of Ornstein are reproduced for comparison.

SAMPLE I (580×11×2 mm., weight 12.5 grams) shows practically no permanent deformation after straining. The specific heat does not change with extension between 0 and 1.9.

TABLE I

SUMMARY OF DATA

Expt. No.	Cm.	Δl	Energy Input Calories	Temp. Increase ° C.	Total Heat Capacity Cal./° C.	Specific Heat Cal./° C./gram	Av. Specific Heat Cal./° C./gram
			SAMPLE I				
1	58	0	0.275	0.0049	5.65	0.375	
2			0.275	0.0049	5.65	0.375	
3			0.275	0.0048	5.75	0.38	
4			0.275	0.0050	5.54	0.365	
5			0.426	0.0072	5.95	0.40	
6			0.426	0.0075	5.72	0.38	
7			0.873	0.0151	5.78	0.385	0.38
8	96 (58)	0.65	0.393	0.0069	5.70	0.38	
9			0.565	0.0098	5.80	0.385	0.385
10	166 (58)	1.9	0.56	0.0102	5.50	0.365	
11			0.56	0.0100	5.58	0.37	
12			0.273	0.049	5.62	0.37	
13			0.79	0.0140	5.65	0.375	0.37
			SAMPLE II				
1	64	0	0.285	0.0058	4.92	0.395	
2			0.287	0.0061	4.73	0.375	
3			0.448	0.0100	4.47	0.35	
4			0.670	0.0140	4.78	0.38	
5			0.407	0.0083	4.92	0.395	
6			0.573	0.0119	4.83	0.385	0.38
7	170 (64)	1.7	0.573	0.0109	5.27	0.43	
8			0.330	0.0063	5.28	0.43	
9			0.560	0.0109	5.16	0.42	
10			0.447	0.0086	5.22	0.425	0.43
11	300 (64)	3.7	0.447	0.0083	5.40	0.445	
12			0.289	0.0054	5.33	0.435	
13			0.440	0.0082	5.37	0.44	
14			0.534	0.0100	5.37	0.44	0.44
15	67	0	0.673	0.0135	4.97	0.40	
16			0.420	0.0081	5.18	0.42	
17			0.482	0.0097	4.99	0.40	
18			0.206	0.0041	5.18	0.42	0.41
19	105 (69)	0.5	0.527	0.0106	4.98	0.40	
20			0.407	0.0079	5.13	0.415	
21			0.374	0.0075	4.98	0.40	
22			0.475	0.0100	4.78	0.38	
23			0.622	0.0128	4.86	0.39	
24			0.289	0.0057	5.07	0.41	0.40
25	220 (71)	2.1	0.425	0.0083	5.13	0.415	
26			0.462	0.0089	5.17	0.42	
27			0.425	0.0084	5.08	0.41	
28			0.613	0.0117	5.25	0.43	
29			0.712	0.0141	5.07	0.41	0.42

SAMPLE II (640×14×1 mm., weight 10.0 grams) shows a marked permanent deformation after straining. At the end of the series of experiments, the length of the band was 710 mm., compared with 640 mm. at the beginning. To give consideration to the possible influence of this change on the specific heat, exten-

sions were tried in the following order: 0, 1.7, 3.7, 0, 0.5, 2.1. The interpolation in Figure 4 seems to indicate a slow increase of the specific heat with the extension, but this increase is near the limits of reproducibility.

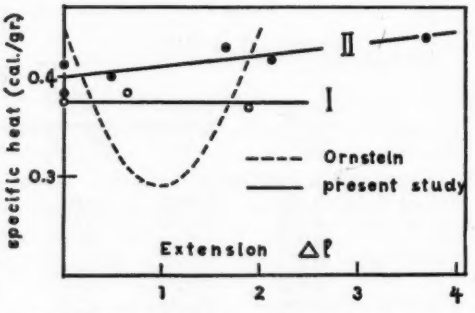

FIG. 4.—Specific heat of samples I and II as a function of extension.

The results obtained with both samples do not confirm the large decrease in specific heat with extension found by Ornstein. Ornstein and his coworkers measured a "mean specific heat" over a temperature interval of 60° C. The transformations which may occur in strained rubber when it is heated to 80° C. and then suddenly cooled may be accompanied by considerable evolution of heat.

A CONTRIBUTION TO THE CHARACTERIZATION OF THE PLASTIC-ELASTIC STATE *

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The manner in which vulcanized rubber can be deformed and yet return almost completely to its original dimensions after the stress is released is a unique and characteristic property. Technically the problem in testing rubber is to evaluate this property and to define it in terms of the factors which are concerned.

To define completely this property of rubber whereby it is susceptible to deformation, it is necessary to know the stress, the elongation, the energy expended, the energy lost, the time and the temperature. The stress, elongation and energy expended are closely related and are characterized by the stress-strain curve, which in turn depends on the time and temperature. In addition, it must be borne in mind that rubber can be deformed either by tension or by pressure, but this will not be discussed further here.

On the other hand a rather puzzling problem will be considered, the solution of which brings out the fact that the three variables involved in any deformation, *viz.*:

(1) The time or frequency.

(2) The temperature.

(3) The interrelated factors: stress, elongation and energy expended, must be varied considerably in order to characterize the phenomena of deformation and that when this is done, unexpected results are obtained.

Figure 1 shows a comparison between a tire tread made of Buna-S and one made of natural rubber subjected to repeated stresses, with the resulting hysteresis effects.

The initial stress-strain curves are approximately the same, but the tread of natural rubber shows the greater hysteresis effect; in fact after ten cycles the difference has become so great that the energy loss is about six times as great for the natural rubber tread as for the Buna-S tread. In addition the elongation of the natural rubber tread has increased to more than twice its initial elongation, whereas the elongation of the Buna-S tread has increased only 12 per cent.

The significance of this experiment lies in the fact that the work capacity of the Buna-S tread is six times as great as that of the natural rubber tread; in other words the Buna-S tread is more stable than the natural rubber tread. Hence such a Buna-S tread would be expected to run at lower temperatures than would the natural rubber tread. Nevertheless, practical experience has shown that this is not true. Moreover these same comparative results are always found in the case of other rubber mixtures, so that the question arises as to which of the variables just mentioned may reverse completely the results

* Translated for *Rubber Chemistry and Technology* from *Kautschuk*, Vol. 15, No. 4, pages 64-68, April 1939. An introductory section on the general mechanical properties of soft vulcanized rubber under different conditions of temperature, rate of extension, etc., as exhibited by its stress-strain curves, hysteresis, etc., is omitted in this translation.

within some other range of measurements and what are the limiting conditions under which such a reversal takes place.

It cannot be the frequency, because data obtained in experiments on static and dynamic hysteresis by Roelig in Leverkusen have shown practically consistent results throughout, and in no case did he observe any reversal of the comparative effects.

Furthermore, since the temperature was the same as in the determination of static hysteresis, which gave the reverse effect, an explanation must be sought in the interrelated factors: stress, elongation and energy expended.

An attempt was made to throw further light on the problem by measuring increases in elongation under different loads by the static method. The technique employed was very simple. A ring-shaped test-specimen was loaded quickly with a weight; under these conditions the test-specimen elongated immediately to a definite degree, and when the load was maintained, the elongation con-

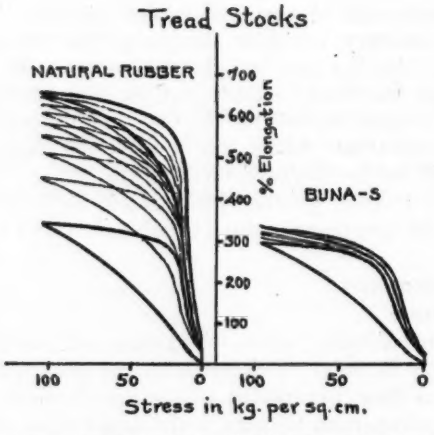

FIG. 1.—Comparison of the hysteresis of Buna-S and natural rubber.

tinued to increase with time, but to a progressively diminishing extent, as may be seen in Figure 2. Figures 3, 4 and 5 show the curves for increasing loads, and bring up the perplexing problem why, at relatively small loads, the greater the load the greater is the increase in elongation, whereas at higher loads the increases in elongation become smaller.

The problem becomes simpler when a logarithmic scale is chosen for the time coördinate. When this is done, it becomes evident that under relatively small loads the total increase in length as a function of time is represented by a straight line. This relation has been found to hold true for all types of rubber mixtures so far tested, and therefore the very unusual situation presents itself that a physical property of soft rubber can be expressed exactly by a simple mathematical function.

This logarithmically linear relation is however true only for relatively small loads, and there is for every vulcanizate a limiting load above which this law is no longer valid. As a matter of fact, in this series of experiments the increase in elongation became progressively greater up to this limiting load, whereas above this particular load only badly reproducible and confusing results were obtained.

This behavior can be explained on the assumption that the complete elongation phenomenon can be resolved into an elastic component and a plastic component. This latter will be designated as "flow." When the load is applied

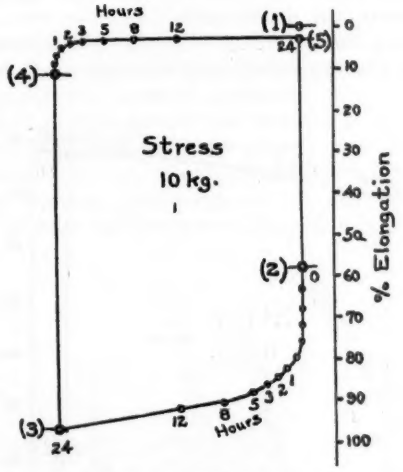

FIG. 2.—Increase in elongation under prolonged stress.

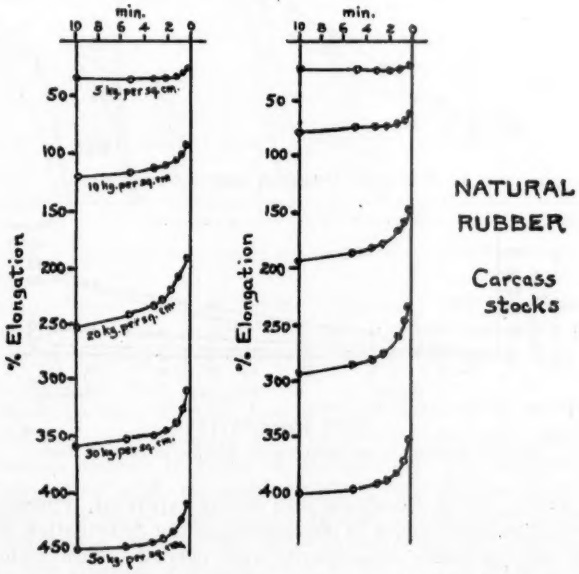
min.
10 8 6 4 2 0
5 kg. per sq. cm.
10 kg. per sq. cm.
20 kg. per sq. cm.
30 kg. per sq. cm.
50 kg. per sq. cm.
% Elongation
50 100 150 200 250 300 350 400 450
NATURAL RUBBER
Carcass stocks

FIG. 3.—Increase in elongation with increase in time of stress.

suddenly, elastic deformation takes place only partially in an infinitely short time, while further elastic deformation, which will be designated as "elastic after-effect," requires a finite time. This elastic after-effect is proportional to the logarithm of the time.

Since, however, with increasing loads the elastic after-effect likewise increases, the relatively large increases in elongation during the initial, very short time intervals under the experimental conditions described can no longer take place, so that the plastic component, which at small loadings is unimportant, then governs the character of the deformation.

This serves to explain the experimental results which have just been described, and also shows that the degree of elongation or, as it has been termed, the

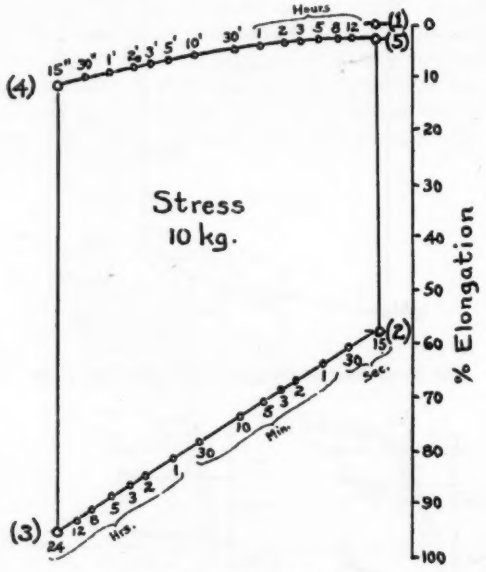

FIG. 4.—Increase in elongation under prolonged stress.

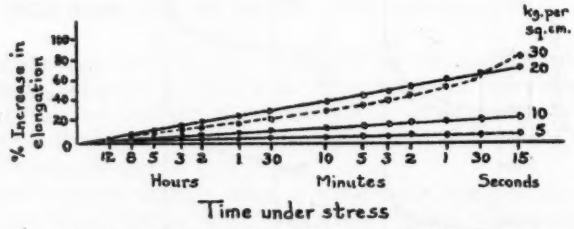

FIG. 5.—Increase in elongation with increase in time of stress.

interrelated factor: stress, elongation and energy expended, represents a variable of particularly great significance in characterizing the deformation of soft rubber.

In view of this, extensive experiments were carried out in addition to those already described, whereby hysteresis curves were obtained over a very wide range of stresses and elongations. These experiments gave interesting results. The recording device on the tensile machine had to be reconstructed on different scales so that the hysteresis loops could still be measured when the work expended was changed as much as twenty-five fold.

Figure 6 shows typical hysteresis curves for various ranges of energy. The latter is expressed in kg. per sq. cm. × percentage elongation. It is obvious

from the form of the loops that the first loop at the right is constructed on the largest scale, the next two loops are on a smaller scale, while the last three loops form another group on a still different scale. The curves in the top row represent a natural rubber vulcanizate, the lower set represent a similar vulcanizate of Buna-S; in each case the lightly drawn line represents the first loop, the thicker line represents the loop obtained after 10 cycles.

An examination of the comparative increases in elongation of the first and tenth loading brings out the essential difference between natural rubber and Buna-S. In the case of natural rubber the increase in elongation for relatively small expenditures of energy is only very small, but above a quite definite amount of energy expended, *i.e.*, above a well-defined range of deformation, the increase suddenly becomes very large. In the case of Buna-S, the relation is just the opposite, for here the increase in elongation is at first relatively great,

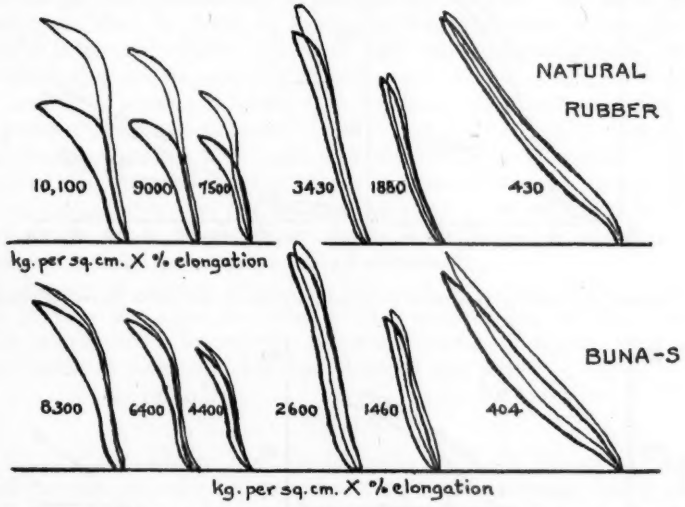

FIG. 6.—Comparison of the hysteresis of Buna-S and natural rubber with increase in energy absorbed.

and then becomes slow. This is shown particularly well in Figures 7 and 8, which show clearly that there is a definite, critical elongation above which natural rubber behaves in just the opposite way from that of Buna-S, and below which it behaves in the same way.

This difference between Buna-S and natural rubber is a property which is independent of the composition of the vulcanizate, and has been found to be true of the widest variety of types of vulcanizates. The sudden jump in the increase in elongation with increasing work expended was found to be true of all vulcanizates prepared from natural rubber, and it was much more evident under these conditions than in the static experiments with constant load. On the contrary, this relation was found not to be true of Buna-S mixtures, for in this case the elongation increased with increasing deformation in a practically linear relation.

If now the areas within the loops in Figure 6 are regarded as the losses in energy with increasing deformations, it will be found that in the case of natural rubber these losses are at first smaller than those of Buna-S, but that subsequently they increase rapidly until they exceed greatly those of Buna-S.

In Figure 8 the areas of the hysteresis loops are represented as percentages of the loads applied, and it is evident that only in the lower range of elongations does Buna-S show greater energy losses than does natural rubber. In the tire tread shown, the curves cross one another at an elongation corresponding to a stress of 35 kg. per sq. cm.; in the carcass stock the elongation corresponds to 40 kg. per sq. cm. Below these stresses, therefore, natural rubber is superior

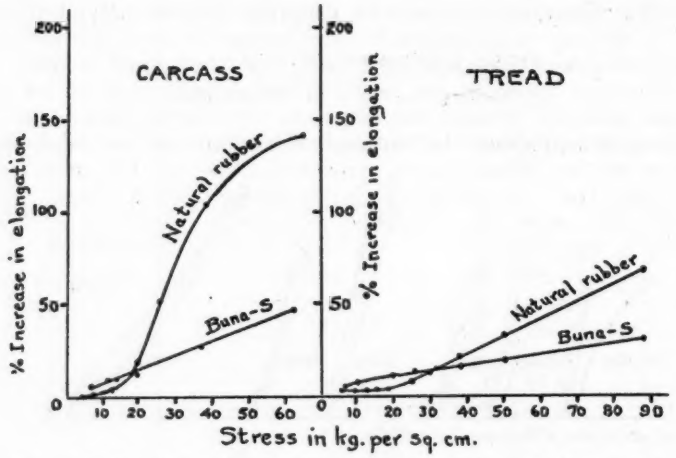

FIG. 7.—Increase in elongation as a result of repeated stresses to increasing degrees of elongation.

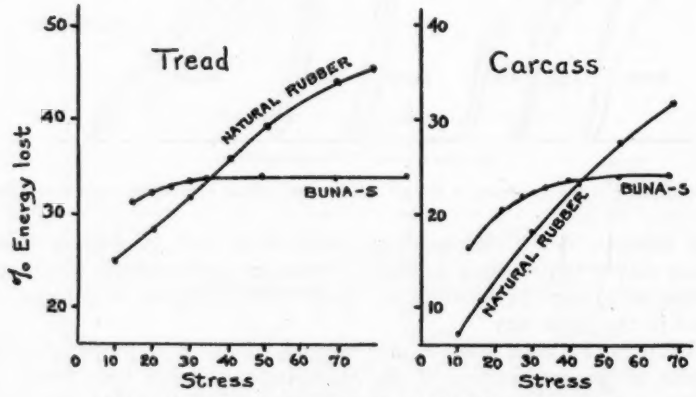

FIG. 8.—Loss of energy with increase in the degree of elongation.

in elasticity and work capacity, whereas above this range of stresses Buna-S is decidedly the better of the two.

This accounts for the results of the experiments described in the beginning and explains its limiting conditions; at the same time the results of these experiments are at variance with the tests carried out by Roelig with the Schopper pendulum machine and with dynamic hysteresis measurements, because in these two methods only very small elongations are involved.

Whether the fact that Buna-S has greater energy capacity under severe conditions of service than has natural rubber is of any technical significance is not a subject of discussion at this point.

THE INFLUENCE OF VULCANIZATION ON THE OXIDIZABILITY OF RUBBER *

VULCANIZING AGENTS OTHER THAN SULFUR

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In a previous publication[1] the influence of vulcanization by sulfur and sulfur compounds on the oxidizability of rubber was shown. The most important conclusion was that, in principle, the higher the proportion of combined sulfur, the greater is the oxidizability. However, with very high proportions, the activity of the sulfur changes, *i.e.*, above a certain upper limiting range, the oxidizability tends towards a plateau, whereas below a lower limiting range the oxidation curve passes through a minimum.

After having obtained these results, it seemed to be of interest to complete the investigation by studying the effects of vulcanization by agents other than sulfur on oxidizability. In the present work we have examined vulcanization by nitro compounds and peroxides, taking as examples *m*-dinitrobenzene, trinitrobenzene and benzoyl peroxide.

This domain of rubber chemistry has been relatively little explored and certain points either have not received final confirmation or have even led to contrary conclusions. Accordingly it seemed useful to review from a purely objective point of view what has been done on this subject.

HISTORY

In 1912 Ostromislensky[2], in his laboratory at the Bogatyr Rubber Co., obtained for the first time a vulcanizate with trinitrobenzene. Later, in a series of publications made in 1915[3], he proved that rubber can be easily vulcanized by nitro compounds and organic peroxides, and he pointed out the following agents as being particularly interesting: 1,3,5-trinitrobenzene, *m*-dinitrobenzene, benzoyl peroxide and also a mixture of 1,3,5,8-tetranitronaphthalene with 25% of nitrobenzene.

According to Ostromislensky, the vulcanizing power of nitro compounds depends on the ability of the active oxygen atom of the nitro group to unite at the double bonds; certain substances are activating, as with vulcanization by sulfur, such as litharge, magnesia, lime and zinc oxide; on the contrary, large proportions of primary and secondary aliphatic amines have a retarding action. Although Ostromislensky states that vulcanization by these nitro agents can take place in the absence of metallic oxides[4], these agents are almost indispensable for vulcanization in a practical way.

On the contrary, with benzoyl peroxide there is no need for additional substances, and even organic accelerators or metallic oxides are contra-indicated. In the case of a simple mixture, vulcanization is brought about more rapidly by this peroxide than by sulfur or nitro compounds.

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* Presented before The Division of Rubber Chemistry at the 98th Meeting of the American Chemical Society at Boston, Massachusetts, September 14, 1939.

After the discovery of these new vulcanizing agents, several authors examined the question, although chiefly from a practical point of view. They confirmed the facts, but found that vulcanizates made in this way have poorer mechanical properties than those of sulfur vulcanizates, and deteriorate so rapidly that they soon become useless.

In the first experiments in this field, Stevens[5], then Porritt[6] were unable to demonstrate the vulcanizing power of dinitrobenzene, because they did not include metallic oxides in their mixes. However, shortly afterwards Stevens[7] had no trouble in vulcanizing mixtures of rubber with di- and with tri-nitrobenzene in the presence of litharge or magnesia, and also confirmed the fact that benzoyl peroxide has a much more rapid action than sulfur.

Bunschoten[8] carried out systematic experiments on vulcanization with nitrobenzene and particularly with *m*-dinitrobenzene. He studied the influence of the proportions of the vulcanizing agent and litharge, as well as the temperature of vulcanization, and measured the mechanical properties of his samples. But he noted that the aging of these compounds was very bad; even at the end of a month the rings prepared for tests on the Schopper dynamometer could be easily broken by hand, whereas their initial tensile strength was about 40 kg. per sq. cm. The author did not believe that such a change in properties was the result of oxidation for, after six months, the acetone extract remained equal to that of crude rubber.

In his book devoted to the science of rubber, Memmler[9] comments on the various results described above and concludes that the new process can in no way replace vulcanization by sulfur because the rapid decline in mechanical properties made it impossible to foresee any practical application.

Meanwhile Sumitomo[10] patented the use of trinitrobenzene for the vulcanization of insulating layers in contact with copper and Ostromislensky[4] pointed out that this product might lead to interesting applications.

Moreover, if one considers the theoretical side of the question, it appears that investigations of this nature are likely to give valuable information on the process of vulcanization; in particular, and we intend to return to this point later, nitro agents give vulcanizates whose resistance to solvents, as Naunton, Jones and Smith[11] noted in connection with oil, is definitely greater than that of sulfur mixtures. This may indicate that different molecular arrangements take place in the different methods of vulcanization.

The theoretical aspects have not, moreover, been neglected.

Twiss[12], like Ostromislensky and Stevens, believed that benzoyl peroxide owed its vulcanizing power to the activity of its oxygen atoms and he noted the parallelism between the action of sulfur and oxygen.

According to Whitby[13], benzoyl peroxide acts in the same way as in the polymerization of vinyl acetate, *i.e.*, as an accelerator of polymerization.

Particular attention should be called to the thorough work of van Rossem, Dekker and Prawirodipoero[14] on vulcanization with benzoyl peroxide particularly cited; they proved that benzoic acid is formed, and came to the conclusion that vulcanization is due to simultaneous dehydrogenation and polymerization of rubber hydrocarbon.

In 1928, Fisher and Gray[15] reviewed the work of Spence and Scott[16] on the chemical unsaturation of ordinary rubber vulcanized by sulfur, work which showed that the percentage of combined sulfur corresponds exactly to the diminution of unsaturation and that, consequently, combination of sulfur consists solely in the addition to the double bonds of rubber. Fisher and Gray studied

whether similar variations could be observed in vulcanization with polynitro compounds or benzoyl peroxide; but they found that the degree of unsaturation in rubber did not change.

On the contrary Blake[17], in new researches on di- and trinitrobenzene, showed that the percentage of combined nitrogen increases with the time of vulcanization and reaches a maximum. He then proved[18], in a study of benzoyl peroxide, that there is an obvious linear relation between the percentage of the combined vulcanizing agent and the unsaturation of rubber hydrocarbon in the compound. According to Blake, the contrary results of Fisher and Gray may be attributed to the incomplete consumption of their reagent. It is impossible to know whether the addition at the double bonds occurs in the same molecule or bridges adjacent molecules. Experiments have, however, shown that the number of saturated double bonds per molecule of vulcanizing agent is higher for nitro compounds than for benzoyl peroxide.

In 1929, Kirchhof[19] felt warranted in concluding that trinitrobenzene is not a true vulcanizing agent and he termed the compounds thus obtained as "pseudo-vulcanizates." However, Garvey[20] then showed that they have the properties of ordinary vulcanized substances.

Finally Wright[21] studied in detail vulcanization by dinitrobenzene and the influence of numerous metallic oxides, and showed with Davies[22] that, contrary to Blake's opinion, hard vulcanizates similar to ebonite can be obtained in this way.

With regard to the more specific problem of aging, the only facts to be added to Bunschoten's seem to be those of van Rossem[14] with respect to benzoyl peroxide and those of Wright[21] with respect to dinitrobenzene. Both noted the poor behavior of their samples in a Geer oven: but natural aging gave irregular results and the correlation with the accelerated test seemed to be made difficult because of blooming at normal temperature.

Thus the net result is in general that these different vulcanizates have poor aging properties. As for the chemistry of this vulcanization, there are a number of imperfectly established points, and in order not to expand unnecessarily the present work, we have limited ourselves to investigating, on the one hand, the influence of the time of vulcanization on oxidizability and on the other hand that of the proportion of the vulcanizing agent, for each of the three agents. Oxidizability was measured in oxygen in darkness, at two temperatures: 20° C. approximately (normal temperature) and 80° C.

m-DINITROBENZENE

According to the literature, in the different mixtures employed in studying this agent, the most frequently used metallic oxide has been litharge. Therefore we prepared a series of litharge mixtures, although, as has already been pointed out, this product possesses considerable proöxygenic activity; also we made other experiments with a series of mixtures containing magnesia.

Table I gives the composition and degrees of vulcanization of the various samples.

As for the properties of these vulcanizates, they show sufficiently the character of the phenomena so that it was not necessary to measure systematically the mechanical properties; it may merely be mentioned that the best samples had a tensile strength of about 120 kg. per sq. cm.

Series DA.—DA_1 (cured 15 minutes) slightly cured, but soft and could be deformed; DA_2 and DA_3 well cured; from DA_4 to DA_7, the samples became more and more brittle: their fracture was lustrous and not tacky.

Series DB.—DB_0 not vulcanized; DB_1, DB_2 and DB_3 well cured; DB_4, DB_5 and DB_6 weak and brittle.

Series DC.—DC_1 and DC_2 soft and tacky; DC_3 and DC_4 semicured; DC_5, DC_6 and DC_7, fairly well cured; but a little soft.

Series DD.—DD_1 and DD_2 soft, other samples well cured.

Finally, to compare oxidizabilities a mixture of smoked sheet 100 and *m*-dinitrobenzene 10 (designated DE) was prepared. This showed no tendency to vulcanize.

TABLE I

Litharge compounds					Magnesia compounds				
	Composition			Minutes of vulcanization at 143° C.		Composition			Minutes of vulcanization at 143° C.
Sample	Smoked sheet	Litharge	*m*-dinitrobenzene		Sample	Smoked sheet	Magnesia	*m*-dinitrobenzene	
DA_0	100	10	10	0	DC_0	100	30	10	0
DA_1	"	"	"	15	DC_1	"	"	"	15
DA_2	"	"	"	30	DC_2	"	"	"	30
DA_3	"	"	"	45	DC_3	"	"	"	45
DA_4	"	"	"	60	DC_4	"	"	"	60
DA_5	"	"	"	90	DC_5	"	"	"	90
DA_6	"	"	"	120	DC_6	"	"	"	120
DA_7	"	"	"	240	DC_7	"	"	"	240
DB_0	100	10	0	30	DD_0	100	30	0	240
DB_1	"	"	2.5	"	DD_1	"	"	2.5	"
DB_2	"	"	5	"	DD_2	"	"	5	"
DB_3	"	"	10	"	DD_3	"	"	10	"
DB_4	"	"	15	"	DD_4	"	"	15	"
DB_5	"	"	20	"	DD_5	"	"	20	"
DB_6	"	"	30	"	DD_6	"	"	30	"

1—Influence of the Time of Vulcanization

a—Litharge compounds (Series DA)

Figure 1 shows the oxidation curves of the eight compounds of the series DA and those of 3 control samples:

DB_0 raw, containing litharge without dinitrobenzene,

DE, containing dinitrobenzene without litharge,

FF containing neither litharge nor dinitrobenezene and made only with smoked sheet milled for the same time as the other stocks.

The oxidizabilities were measured at 80° C, using in each case a weight corresponding to 1 gram of rubber.

The vulcanized samples showed similar oxidizabilities: and in no case did the oxidizability increase indefinitely with the time of vulcanization.

The phenomenon is more obvious if we represent (on Figure 1A), as a function of the time of vulcanization, the oxidation values taken from the curves of Figure 1 for a determined value of the abscissae of that figure, corresponding to the duration of oxidation, for 10 and 20 hours respectively. Oxidizability first increases rapidly with the time of vulcanization, reaches a maximum and then decreases slightly; this decrease may be attributed to the fact that the more brittle and harder the mixture, the less permeable it becomes.

One cannot help comparing the maximum oxidizability thus observed with the results obtained by Blake[17] in the determination of combined nitrogen.

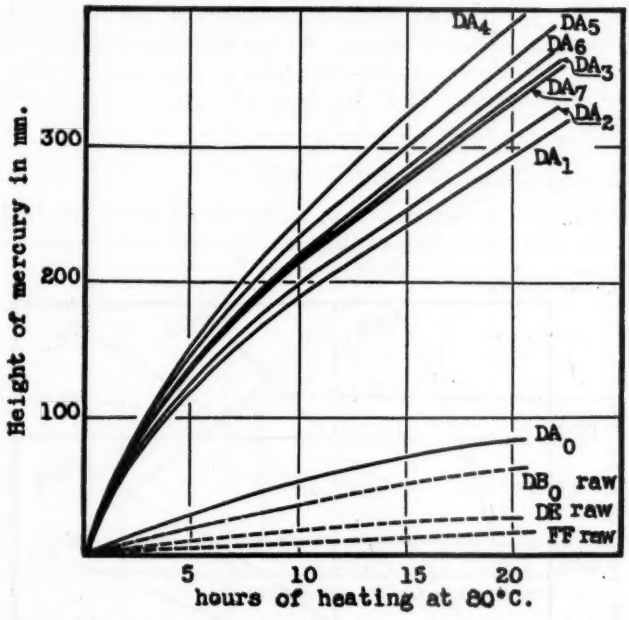

FIG. 1.—Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of *m*-dinitrobenzene mixtures accelerated by litharge.

DB_0 (raw) contains litharge without dinitrobenzene, DE dinitrobenzene without litharge and FF is smoked sheet alone.

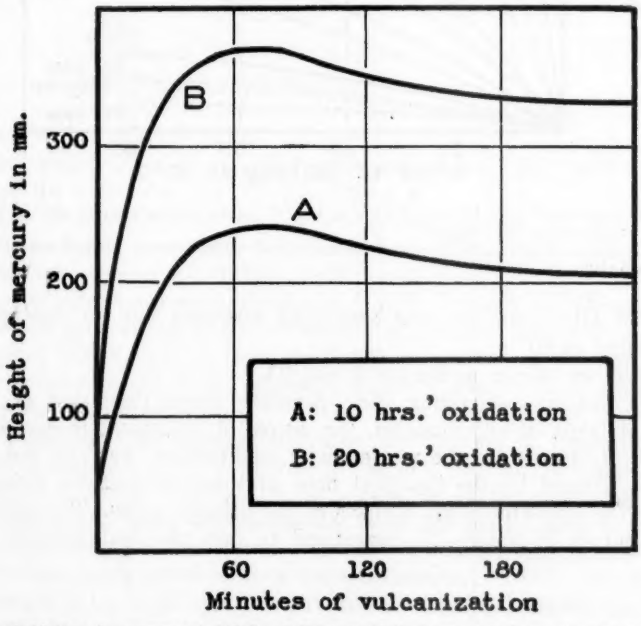

FIG. 1A.—Oxidation in oxygen at 80° C. of litharge-dinitrobenzene vulcanizates (series DA) as a function of the time of vulcanization at 143° C.

These curves reproduce, in another system of variables, the results shown in Figure 1 and correspond to 10 and 20 hours' oxidation.

Blake showed that the percentage of combined nitrogen increases with the time of vulcanization and reaches a plateau. We are therefore justified in concluding that oxidizability increases with the proportion of combined nitrogen, *i.e.*, with the degree of vulcanization. Thus, the same phenomenon was observed in the case of sulfur.

b—Magnesia compounds (Series DC)

The oxidizabilities (in each case with quantities corresponding to 1 gram of rubber), of the eight compounds of the series DC and control samples FF, DE

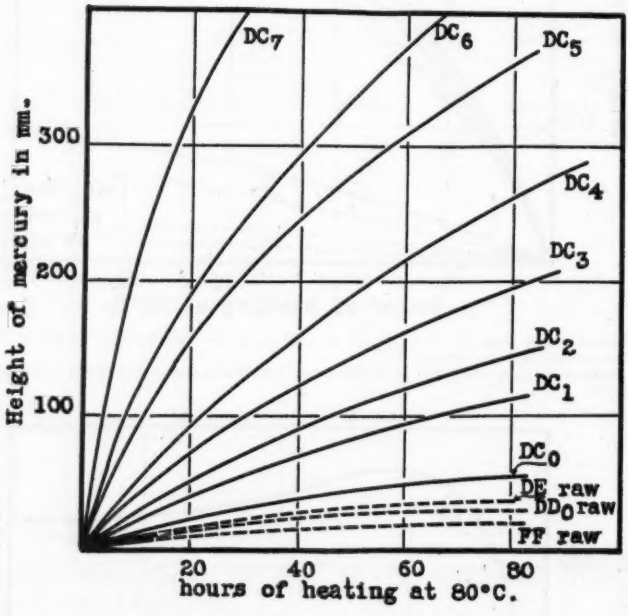

FIG. 2.—Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of *m*-dinitrobenzene mixtures accelerated by magnesia.
DD_0 (raw) contains magnesia without dinitrobenzene, DE dinitrobenzene without magnesia and FF is smoked sheet alone.

and uncured DD_0 (this last one containing magnesia but no dinitrobenzene) were measured at 80° C.

The results are shown in Figures 2 and 2A.

Magnesia has an accelerating effect definitely lower than that of litharge; also, after 4 hours of vulcanization, the degree of vulcanization corresponding, in the case of litharge, to the maximum of oxidizability, was still not reached. This was confirmed by the fact that none of these vulcanizates obtained was brittle like the over-vulcanized samples of the litharge series. The continuously ascending curves of Figure 2A correspond to only the first part of those of Figure 1A.

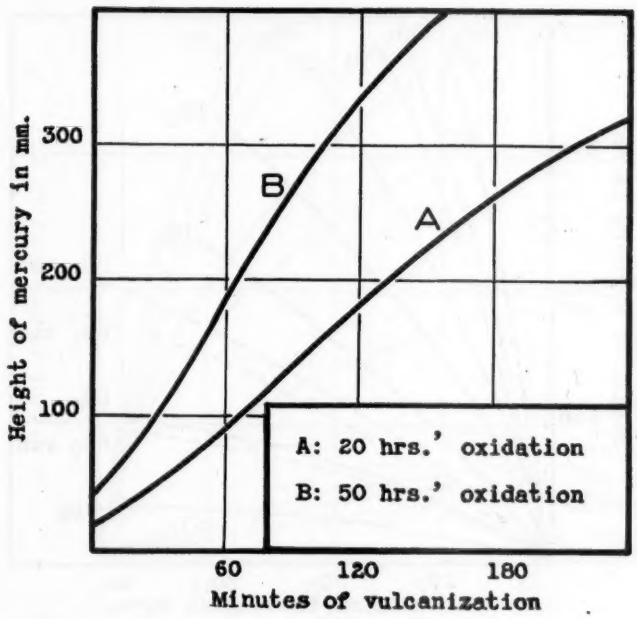

FIG. 2A.—Oxidation in oxygen at 80° C. of magnesia-dinitrobenzene vulcanizates (series DC) as a function of the time of vulcanization at 143° C.
These curves reproduce, in another system of variables, the results shown in Figure 2 and correspond to 20 and 50 hours' oxidation.

2—INFLUENCE OF THE PROPORTION OF DINITROBENZENE

The results obtained with litharge or magnesia are absolutely parallel.

Two sets of measurements were made:

(1) the oxidizabilities of litharge mixtures (series DB) before and after vulcanizing for 30 minutes at 143° C. (see Figure 3).

(2) the oxidizabilities of magnesia mixtures (series DD), before and after vulcanizing for 4 hours at 143° C. (see Figure 4).

Since the oxidizabilities of the raw stocks were nearly the same, only the curves corresponding to samples Nos. 1 and 6 are shown on the graph, as these are the limiting cases of the curves of intermediate samples.

The results are shown more clearly in Figures 3A and 4A, the abscissae of which are the proportions of dinitrobenzene in the mixtures and the ordinates the oxidation values derived from the family of curves of the corresponding figure for definite values of the abscissae of that figure, *i.e.*, 2, 5 and 10 hours' heating in oxygen, respectively.

It is obvious that the oxidizability does not increase in proportion to the percentage of dinitrobenzene, but seems to rise to a plateau. It would have been interesting to represent oxidizability as a function of the percentage of combined nitrogen, but these determinations were not made. But if the results obtained with sulfur are taken into account (see Fig. 15A in reference no. 1), the curve would be expected to have the same shape.

With regard to the oxidizability of raw mixtures (dotted curves) the following points should be noted.

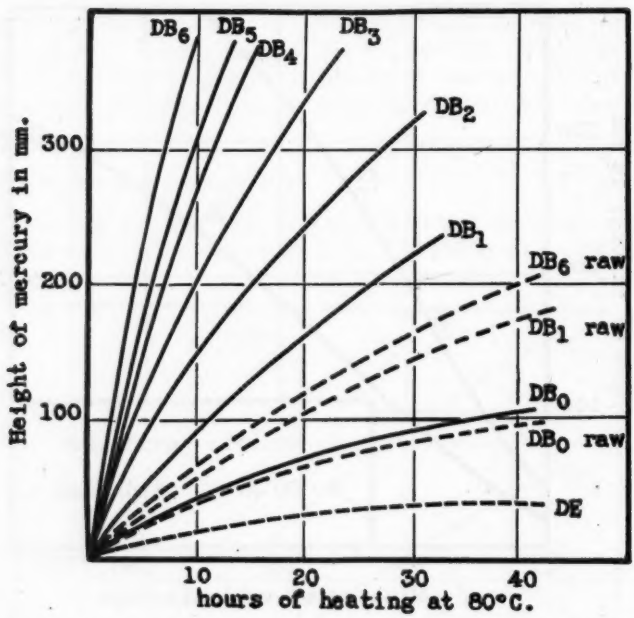

FIG. 3.—Influence of the proportion of *m*-dinitrobenzene on the oxidizability at 80° C. of dinitrobenzene-litharge mixtures, before and after vulcanizing for 30 minutes at 143° C.
Dotted curves: raw stocks.
Continuous curves: vulcanized stocks.
DE contains 10 parts of dinitrobenzene, but no litharge.

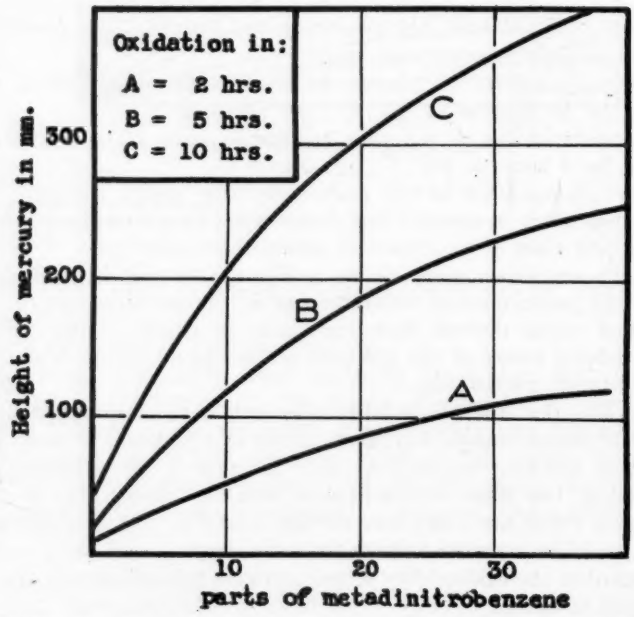

FIG. 3A.—Oxidation in oxygen at 80° C. of litharge-dinitrobenzene mixtures (series DB) as a function of the proportion of dinitrobenzene.
The curves reproduce, in another system of variables, the results shown in Figure 3 and correspond to 2, 5 and 10 hours' oxidation.

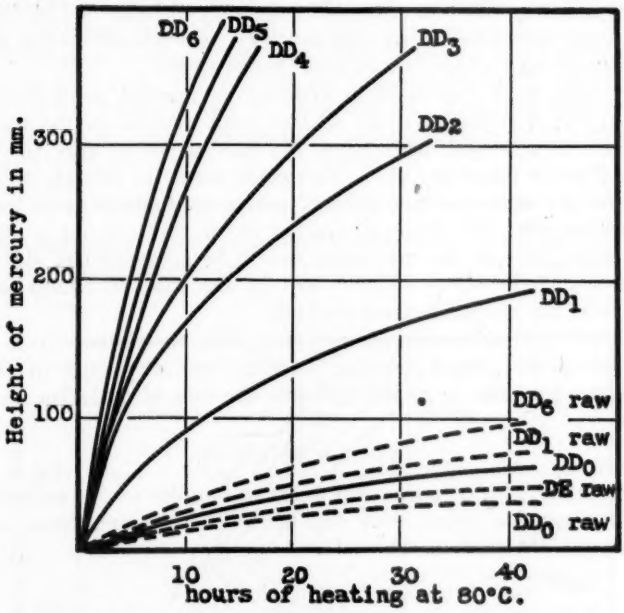

FIG. 4.—Influence of the proportion of *m*-dinitrobenzene on the oxidizability at 80° C. of dinitrobenzene-magnesia mixtures, before and after vulcanizing for 4 hours at 143° C.
Dotted curves: raw stocks.
Continuous curves: vulcanized stocks.
DE contains 10 parts of dinitrobenzene but no magnesia.

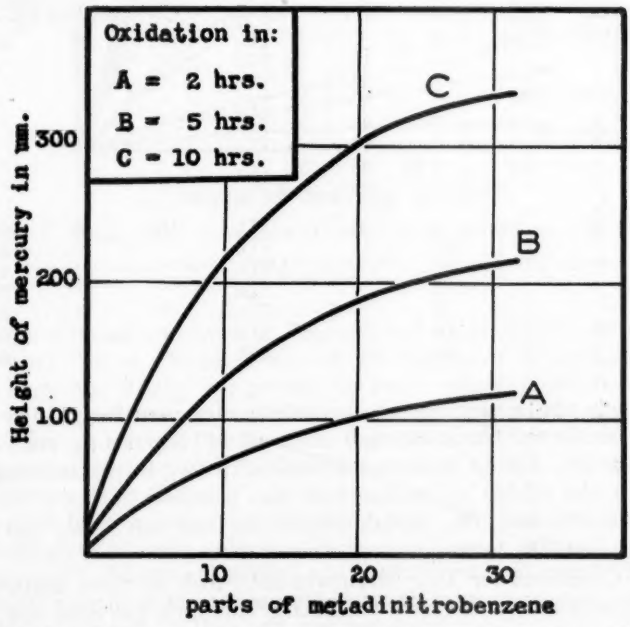

FIG. 4A.—Oxidation in oxygen at 80° C. of magnesia-dinitrobenzene mixtures (series DD) as a function of the proportion of dinitrobenzene.
The curves reproduce, in another system of variables, the results shown in Figure 4 and correspond to 2, 5 and 10 hours' oxidation.

In the first place, the raw samples containing litharge are definitely more oxidizable than those accelerated with magnesia, which confirms the proöxygenic effect of litharge which has already been demonstrated.

Secondly, with these two series of mixtures an increase in oxidizability, relatively slight but nevertheless quite definite, with increase in the proportion of dinitrobenzene is observed, whereas, in the case of sulfur, only the percentage of combined sulfur plays any part. This result seems to indicate a proöxygenic action of dinitrobenzene on raw rubber; moreover dinitrobenzene may be considered as a peroxide, NO_2 being a peroxide group, and it is not at all surprising that the oxidizability of the raw mixes should be a function of the proportion of the agent introduced, as will be seen in the case of trinitrobenzene and still more so in the case of benzoyl peroxide.

Note.—These different series of tests were also made similarly in oxygen at normal temperature (about 20° C.). In each case, the order of classification of samples was the same as at 80° C.; only the rate of oxidation was slower.

TRINITROBENZENE

In the same way, we prepared two series of samples as for *m*-dinitrobenzene, one with litharge, the other with magnesia. Their compositions and degrees of vulcanization are given in Table II.

TABLE II

Litharge compounds					Magnesia compounds				
	Compounds			Minutes of vulcanization at 143° C.		Compounds			Minutes of vulcanization at 143° C.
Sample	Smoked sheet	Litharge	Trinitrobenzene		Sample	Smoked sheet	Magnesia	Trinitrobenzene	
TA_0	100	10	5	0	TC_0	100	30	5	0
TA_1	"	"	"	10	TC_1	"	"	"	10
TA_2	"	"	"	20	TC_2	"	"	"	20
TA_3	"	"	"	30	TC_3	"	"	"	30
TA_4	"	"	"	40	TC_4	"	"	"	40
TA_5	"	"	"	50	TC_5	"	"	"	50
TA_6	"	"	"	60	TC_6	"	"	"	60
TA_7	"	"	"	120	TC_7	"	"	"	120
TB_0	100	10	0	30	TD_0	100	30	0	60
TB_1	"	"	0.5	"	TD_1	"	"	0.5	"
TB_2	"	"	1	"	TD_2	"	"	1	"
TB_3	"	"	3	"	TD_3	"	"	3	"
TB_4	"	"	5	"	TD_4	"	"	5	"
TB_5	"	"	10	"	TD_5	"	"	10	"
TB_6	"	"	15	"	TD_6	"	"	15	"

Again, only the appearance of the vulcanizates need be pointed out. The best samples showed tensile strength of about 140 kg. per sq. cm.

Series TA-TA_1 already cured, but a little soft; TA_7, brittle and fragile; intermediate samples pliable and elastic, with high permanent sets.

Series TB-TB_1 and TB_2 slightly cured, but still soft; TB_3 and TB_4 well cured; TB_5 and TB_6 brittle.

Series TC—Except for TC_0, which was not cured, all these mixtures vulcanized; all were a little softer than the litharge mixtures, but none was brittle.

Series TD—TD_1 and TD_2 slightly cured, but still soft; others well cured, except TD_6 which was slightly brittle.

Finally, to compare oxidizabilities, a mixture of smoked sheet 100 and trinitrobenzene 5, was prepared. The raw sample is designated TE_0; another portion, TE_1, was cured for 1 hour at 143° C.; although soft it showed incipient vulcanization. This seems to prove the ability of trinitrobenzene to vulcanize without an activator.

1—Influence of the Time of Vulcanization

These measurements were made under the same conditions as those for similar mixtures with dinitrobenzene, accelerated with litharge and magnesia, respectively.

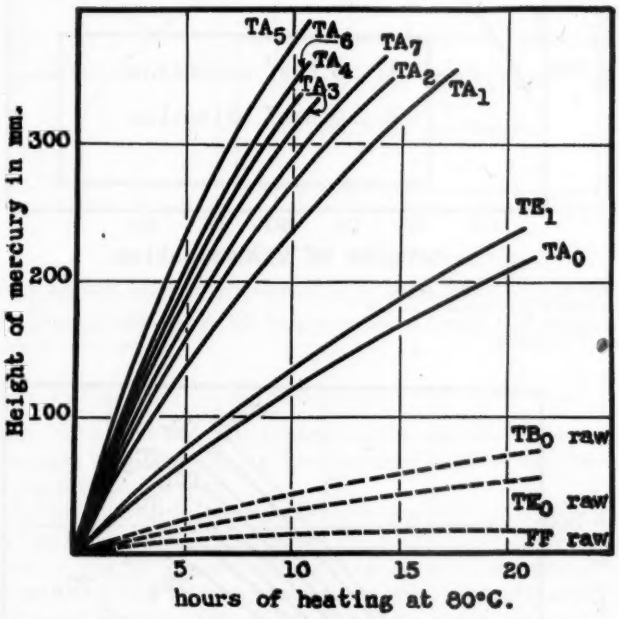

Fig. 5.—Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of litharge-trinitrobenzene mixtures.
TB_0 (raw) contains litharge without trinitrobenzene; TE_0 (raw) and TE_1 (cured for 1 hour at 143° C.) trinitrobenzene without litharge; FF is smoked sheet alone.

The results obtained are shown in Figures 5 and 5A for samples with litharge-trinitrobenzene, and in Figures 6 and 6A for samples with magnesia-trinitrobenzene. They are strictly comparable to those observed for dinitrobenzene and lead to the same conclusions. However, since the vulcanizing action of trinitrobenzene is definitely more rapid than that of dinitrobenzene, it was possible to show the maximum oxidizability reached by the magnesia-trinitrobenzene mixtures (Fig. 6A).

On the other hand, it may be noted that sample TE_1 without metallic oxide, which showed signs of slight vulcanization, was made very oxidizable by heating for 1 hour at 143° C.; its oxidizability was similar to that of sample TC_6 which, with the same content of trinitrobenzene, but with magnesia as well, was vulcanized for the same length of time and was well cured.

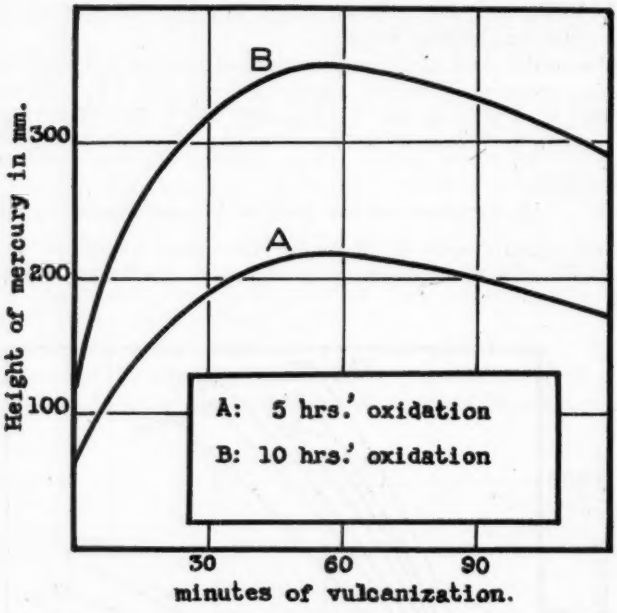

FIG. 5A.—Oxidation in oxygen at 80° C. of litharge-trinitrobenzene mixtures (series TA) as a function of the time of vulcanization at 143° C.

These curves reproduce, in another system of variables, the results shown in Figure 5 and correspond to 5 and 10 hours' oxidation.

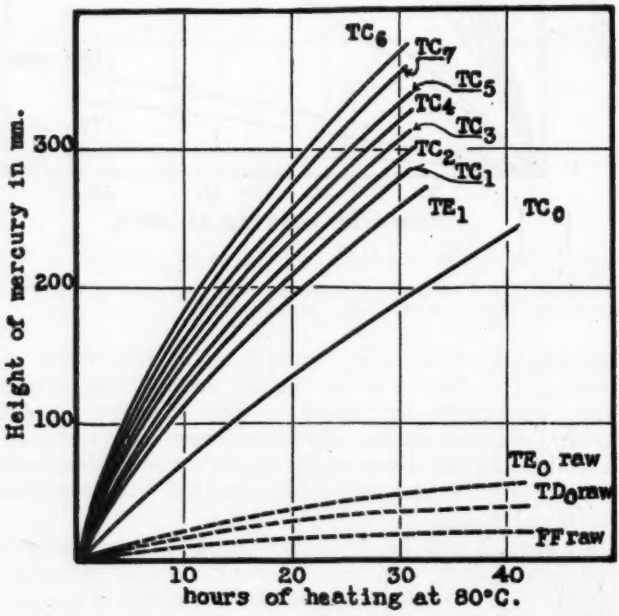

FIG. 6.—Influence of time of vulcanization at 143° C. on the oxidizability at 80° C. of magnesia-trinitrobenzene mixtures.

TD_0 (raw) contains magnesia without trinitrobenzene; TE_0 (raw) and TE_1 (cured for 1 hour at 143° C.) trinitrobenzene without magnesia; FF is smoked sheet alone.

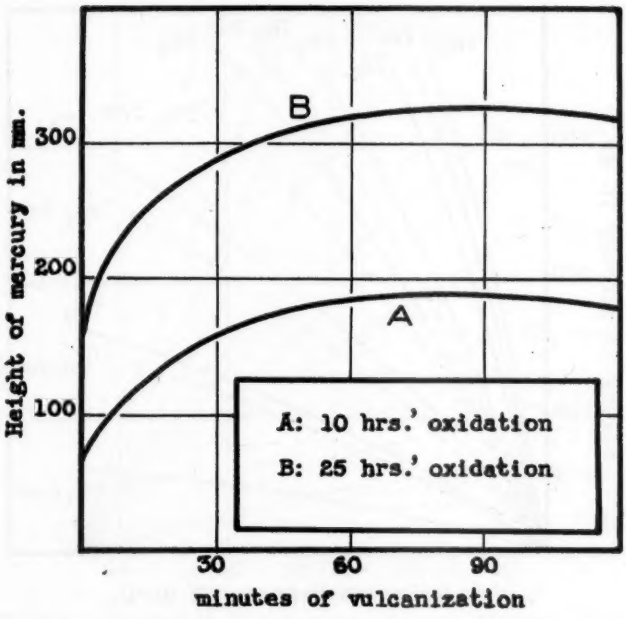

FIG. 6A.—Oxidation in oxygen at 80° C. of magnesia-trinitrobenzene mixtures (series TC) as a function of the time of vulcanization at 143° C.
These curves reproduce, in another system of variables, the results shown in Figure 6 and correspond to 10 and 25 hours' oxidation.

2—INFLUENCE OF THE PROPORTION OF TRINITROBENZENE

Here again, both with the TB litharge series and the TD magnesia series, the measurements were made under the same conditions as with the corresponding dinitrobenzene compounds.

The results for the litharge-trinitrobenzene samples are shown in Figures 7 and 7A, and in Figures 8 and 8A for the magnesia-trinitrobenzene samples.

The curves of Figures 7A and 8A show clearly that the oxidizability of the cured mixtures tends to a plateau, precisely as with trinitrobenzene vulcanizates.

It may be noted that the oxidizability of the raw mixes increased with increase in the proportion of trinitrobenezene; hence the latter also acts as a proöxygenic agent. Nevertheless examination of the oxidation curves (dotted) of the raw stocks in Figure 7 calls for some comment: in effect, they show that, with progressive addition of trinitrobenzene, the oxidizability increases much more than for series DB, DD or TD. There is every reason to conclude that to the proöxygenic effect of trinitrobenzene is added the influence of heating. Since the vulcanizing action of trinitrobenzene with litharge is very rapid, heating at 80° causes incipient vulcanization and an increase of oxidizability.

This hypothesis was confirmed by measuring oxidizabilities at normal temperature; under these conditions, the distances between the different oxidation curves remain small and of the same type as those of the measurements of the corresponding series DB, DD, TD.

Note.—Except in the case of the raw mixes of series TB, noted above, oxidation tests made at normal temperature gave results exactly parallel to those obtained at 80° C.

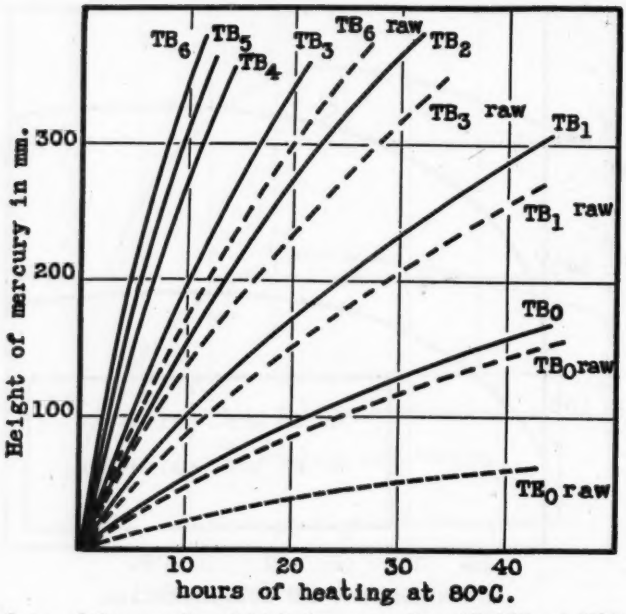

FIG. 7.—Influence of the proportion of trinitrobenzene on the oxidizability at 80° C. of trinitrobenzene-litharge mixtures before and after vulcanizing for 30 minutes at 143° C.
Dotted curves: raw stocks.
Continuous curves: vulcanized stocks.
TE_0 contains 5 parts of trinitrobenzene but no litharge.

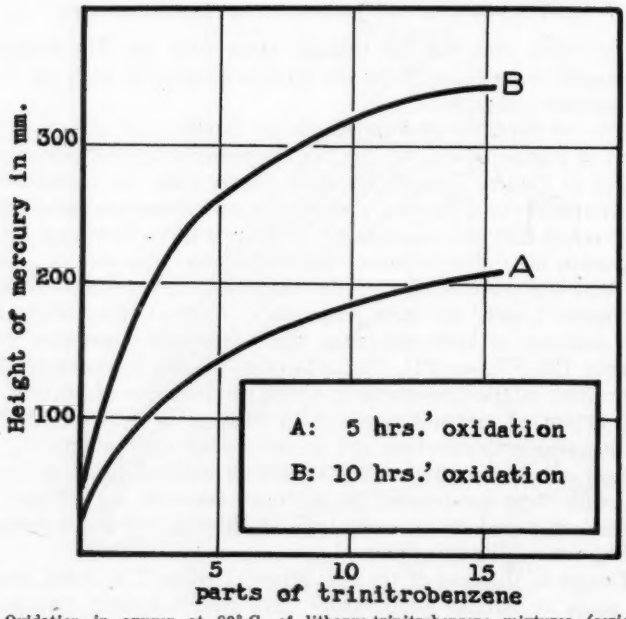

FIG. 7A.—Oxidation in oxygen at 80° C. of litharge-trinitrobenzene mixtures (series TB) as a function of the proportion of trinitrobenzene.
The curves reproduce, in another system of variables, the results shown in Figure 7 and correspond to 5 and 10 hours' oxidation.

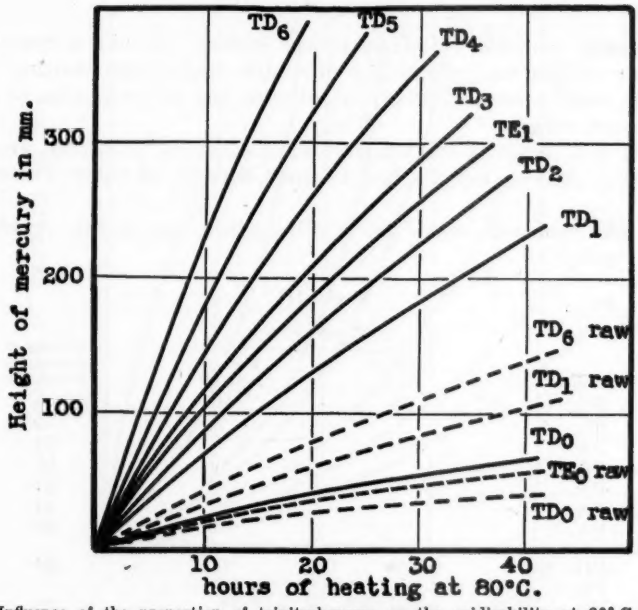

FIG. 8.—Influence of the proportion of trinitrobenzene on the oxidizability at 80° C. of trinitrobenzene magnesia, mixtures, before and after vulcanizing for 1 hour at 143° C.
Dotted curves: raw stocks.
Continuous curves: vulcanized stocks.
TE_0 contains 5 parts of trinitrobenzene, but no magnesia.

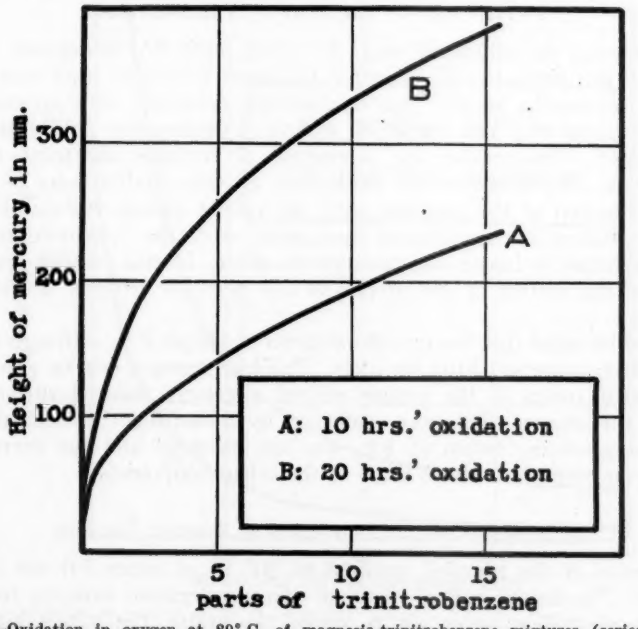

FIG. 8A.—Oxidation in oxygen at 80° C. of magnesia-trinitrobenzene mixtures (series TD) as a function of the proportion of trinitrobenzene.
The curves reproduce, in another system of variables, the results shown in Figure 8 and correspond to 10 and 20 hours' oxidation.

BENZOYL PEROXIDE

Since benzoyl peroxide vulcanizes rubber without the aid of any other ingredient, we studied the oxidizability of simple smoked sheet-benzoyl peroxide mixtures, in which case the time of vulcanization and the proportion of vulcanizing agent were varied.

Table III is a record of the samples; the mechanical properties were not all measured, but the best samples had a tensile strength of about 90-100 kg. per sq. cm.

All samples were well cured, except PB_1, which was slightly cured, and of course PA_0 and PB.

TABLE III

Sample	Composition: Smoked sheet	Composition: Benzoyl peroxide	Minutes of vulcanization at 143° C.
PA_0	100	10	0
PA_1	"	"	5
PA_2	"	"	10
PA_3	"	"	15
PA_4	"	"	20
PA_5	"	"	30
PA_6	"	"	60
PB_0	100	0	30
PB_1	"	2.5	"
PB_2	"	5	"
PB_3	"	10	"
PB_4	"	15	"
PB_5	"	20	"

1—Influence of the Time of Vulcanization

By comparing the oxidizabilities at 80° C. of series PA, the system of curves in Figure 9 was obtained. The result is the exact reverse of what was observed for other vulcanizing agents: the oxidizability decreased with increase in the time of vulcanization. This should be attributed to the great proöxygenic power of peroxides[24]. The greater the percentage of peroxide, the more rapid the autoöxidation. So, whatever the mechanism of vulcanization may be, there is always a reaction of the peroxide with the rubber during vulcanization; thus a certain amount of the reagent disappears, with the formation of benzoic acid[14], which has no longer any proöxygenic effect. In this way, the progressive lowering of the content of the samples in free peroxide explains the decrease of oxidizability.

It should be noted that the rate of oxidation of sample PA_0, although extremely rapid at first, decreased little by little. This phenomenon can be attributed to the fact that fusion of the sample offered a greatly reduced surface to the action of the oxygen. This was confirmed by measuring the oxidizabilities at normal temperature; fusion of PA_0 was not observed and the corresponding curve was in every case above those of the other compounds.

2—Influence of the Proportion of Benzoyl Peroxide

The curves of the samples, oxidized at 80° C, of series PB are shown on Figure 10. The dotted curves represent the unvulcanized samples (only three have been plotted in order not to crowd the graph, the others being intermediate).

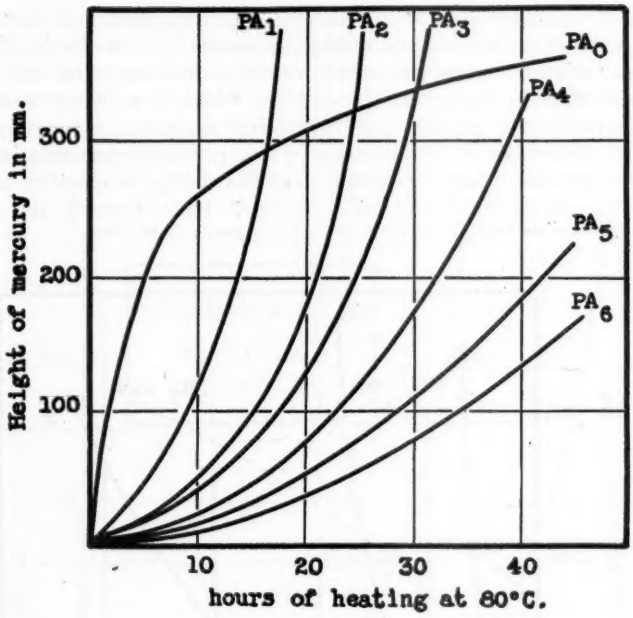

FIG. 9.—Influence of the time of vulcanization at 143° C. on the oxidizability at 80° C. of benzoyl peroxide mixtures.

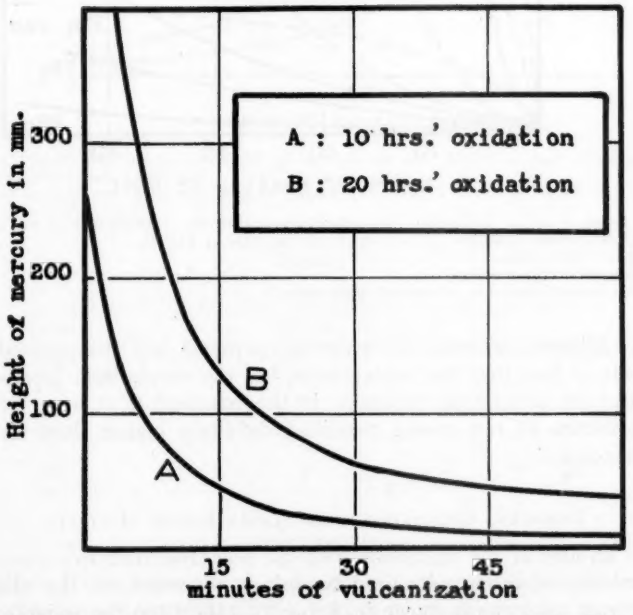

FIG. 9A.—Oxidation in oxygen at 80° C. of benzoyl peroxide mixtures (series PA) as a function of the time of vulcanization at 143° C.

These curves reproduce, in another system of variables, the results shown in Figure 9 and correspond to 10 and 20 hours' oxidation.

Instead of tending towards a maximum, the oxidizability of the vulcanized compounds seems to approach a vertical asymptote, as shown in Figure 10A. As all these mixtures were vulcanized for the same length of time with different proportions of peroxide, the portion which has disappeared may be regarded as practically the same for the different samples: thus the oxidizability increased in proportion to the quantity of free peroxide remaining in the compound. Nevertheless, beyond a certain limit the change in quantity of peroxide influences the oxidizability less and less, as it tends towards the asymptote indicated.

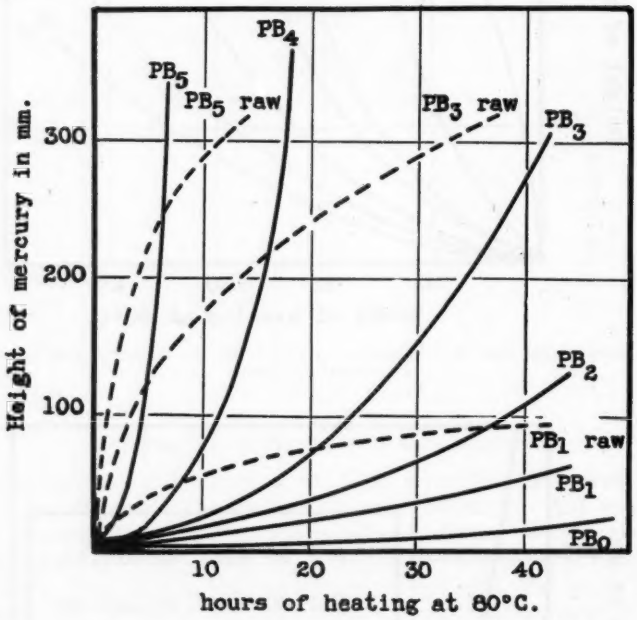

FIG. 10.—Influence of the proportion of benzoyl peroxide on the oxidizability at 80° C. of benzoyl peroxide mixtures, before and after vulcanizing for 30 minutes at 143° C.
Dotted curves: raw stocks.
Continuous curves: cured stocks.
PB_0, without benzoyl peroxide, is smoked sheet alone.

The unvulcanized mixtures, in which no peroxide had disappeared, oxidized more quickly at first than the vulcanizates, but the curves then became inflected as a result of the melting phenomenon. In the experiments at room temperature, the oxidizabilities of raw stocks remained definitely higher than those of the cured compounds.

REMARKS: COMPARISON WITH SIMPLE SULFUR MIXTURES

To have an idea of the oxidizability of the preceding mixtures compared with the oxidizability of those vulcanized by sulfur, we measured the oxidizabilities of the series of compounds shown in Table IV. Here too the weights are based on 1 gram of actual rubber.

The time of vulcanization and the proportion of the vulcanizing agent were not the same in all cases, for we endeavored to make this comparison by choosing from each series the mixture with the best mechanical properties.

The oxidation curves obtained are shown on Figure 11. It can be seen that, except for PB_2 the properties of which were peculiar, the oxidizability of the different samples lay between that of the sulfur mixtures, with and without litharge.

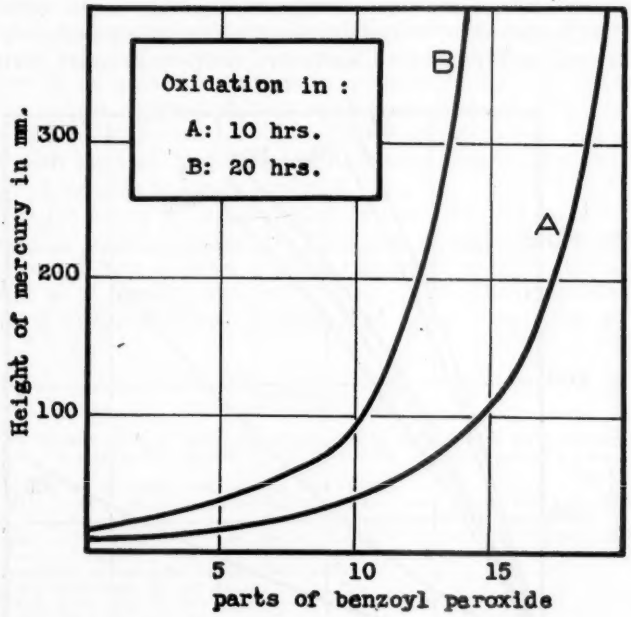

FIG. 10A.—Oxidation in oxygen at 80° C. of benzoyl peroxide mixtures (series PB) as a function of the proportion of benzoyl peroxide.

These curves reproduce, in another system of variables, the results shown in Figure 10 and correspond to 2, 10 and 20 hours' oxidation.

TABLE IV

Sample	Composition						Time of vulcanization at 143° C.
	Smoked sheet	Sulfur	Dinitrobenzene	Trinitrobenzene	Benzoyl peroxide	Litharge	Magnesia	
S	100	6						6 hrs.
SL	100	6				10		30′
DB_2	100		5			10		30′
DD_2	100		10				30	4 hrs.
TB_2	100			5		10		30′
TD_4	100			5			30	60′
PB_2	100				5			30′

CONCLUSIONS

The study of the influence of vulcanization by polynitrobenzenes and by benzoyl peroxide on the oxidizability of rubber is complicated by the proöxygenic action of these products; with benzoyl peroxide this influence is preponderant and alters completely the results to be expected from those obtained with sulfur and nitro compounds.

Nevertheless two general conclusions can be drawn from this preliminary study.

First, none of the measurements indicate a minimum point in the oxidizability comparable to that for small percentages of sulfur; even, the shape of the curves seems to bar such a possibility. Moreover in view of their peroxidic character, it seems improbable that the compounds studied, could have any antioxygenic action; the phenomenon of minimum oxidizability is therefore peculiar to sulfur.

In the second place, as with vulcanization by sulfur, the oxidizability does not increase indefinitely with the time of vulcanization; but seems rather to be a function of the proportion of vulcanizing agent which has combined. A maximum point in the oxidizability observed with nitro compounds agrees perfectly with

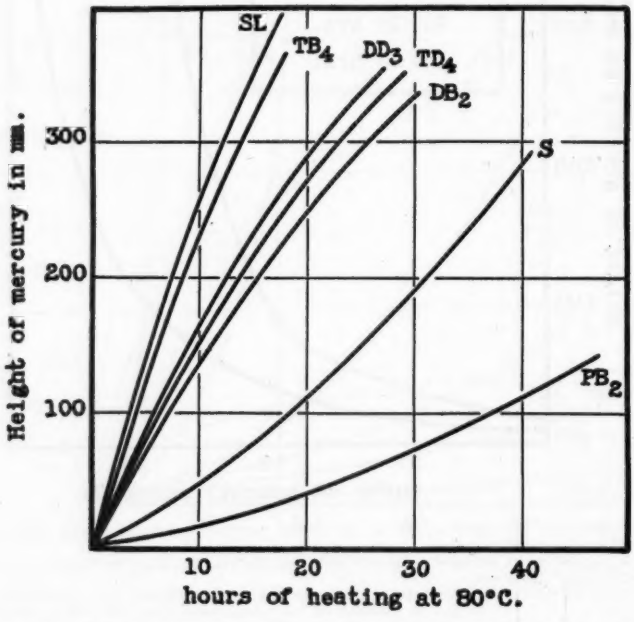

FIG. 11.—Comparison between oxidizabilities at 80° C. of mixtures vulcanized with different agents: S: sulfur; SL: sulfur-litharge; DB_2: dinitrobenzene-litharge; DB_3: dinitrobenzene-magnesia; TB_4: trinitrobenzene-litharge; TD_4: trinitrobenzene-magnesia; PB_2: benzoyl peroxide.

Blake's results[17], and indicates the existence of a maximum point in the combined nitrogen. As for benzoyl peroxide compounds, the recent conclusions of the same author[18] on the unsaturation of these compounds seem to prove that they would follow the same rule as the others if the influence of uncombined peroxide could be eliminated.

In general then, it may be said that the oxidizability of rubber is a function of the combination or the transformation which it undergoes in the process of vulcanization, such a change being governed by the quantity of vulcanizing agent transformed.

Finally, it should be noted that, based on a comparison of the oxidizabilities of the mixtures studied with those of simple sulfur mixtures, the values observed are not at all impossible; for there seems to be no theoretical reason why the

addition of suitable ingredients should not increase the resistance to oxidation of these vulcanizates to the same extent that ordinary antioxygens increase the resistance of sulfur vulcanizates.

RÉSUMÉ

In completion of previous work on vulcanization by sulfur, the oxidizability of rubber containing vulcanizing agents other than sulfur, *viz.*, *m*-dinitrobenzene, trinitrobenzene and benzoyl peroxide, was determined by the manometric method. This study was complicated by the proöxygenic action of these compounds. However, the following general conclusions may be drawn.

(1) None of the measurements shows a minimum point in the oxidizability comparable to that shown with very small percentages of sulfur.

(2) As with vulcanization by sulfur, the oxidizability does not increase progressively with the time of vulcanization, but appears to be a function of the percentage of vulcanizing agent combined.

(3) A comparison of the oxidizabilities of these different mixtures with those of simple sulfur mixtures shows that their rate of oxidation is not very great. It seems possible then to lower it, with the aid of suitable ingredients, to the same extent as is possible with antioxygens. Consequently there is no reason for not using oxidants as well as sulfur and sulfur compounds as vulcanizing agents.

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PROPERTIES OF HARD RUBBER

VII. MEASUREMENT OF PLASTIC FLOW AS AFFECTED BY TEMPERATURE *

H. F. Church and H. A. Daynes

INTRODUCTION

In a previous report (*J. Rubber Research* 5, 11 (1936) attention was drawn to the importance of tests on plastic yield as a means of (*a*) evaluating an insulating material to be used at high temperatures; (*b*) checking the degree of vulcanization in production control, and (*c*) studying the structure of hard rubber. The objections to a rising temperature method, such as the Martens method adopted by the Verband Deutscher Elektrotechniker, were pointed out and some preliminary tests were described in which plastic deformation was produced by a torsional strain applied to a vertical strip of material immersed in a bath of liquid which could be maintained at various steady temperatures. Determinations were made of (*a*) permanent set after subjection to a given strain, and (*b*) rate of yield under a stress sufficient to produce a given initial torsional strain; but it was pointed out that a method of measuring the rate of deformation under constant torsional stress was desirable. This method has now been developed and forms the subject of this report.

Of the methods which have been used by other observers in the study of the plastic flow of hard rubber, the cantilever, three-point loading and four-point loading methods of applying a bending stress, if used under a series of steady temperature conditions, might all be used to give absolute data as to the plastic properties of a material. In particular the four-point loading apparatus, of which the Martens apparatus is a very well-known form, has some attractive features. However, experience with this apparatus in its standardized form has revealed the following points which make it inconvenient for use in the present research on hard rubber:

(1) The loading device is too heavy for specimens cut from thin sheets (5 mm. thick).

(2) The apparatus is bulky and requires a large oven.

(3) Considerable time is required to readjust the temperature and to ensure that the specimen has acquired a known temperature.

(4) Rate of flow from a position of zero strain cannot be measured, since the device for actuating the pointer which indicates the deflection puts a small initial load on the sample. This is no disadvantage in the standard V.D.E. test, but introduces difficulties in studying the fundamental properties of the material.

(5) Modifications of the oven are required if the load is to be applied or removed without disturbing the temperature conditions.

(6) When in a very plastic condition the vertically disposed test-piece will collapse under the weight of the stressing device which is applied to its upper end. This limits the range of temperatures over which the material can be studied.

* Reprinted from the *Journal of Rubber Research*, Vol. 8, No. 4, pages 41-51, April 1939.

To overcome these difficulties it was decided that the apparatus described should be developed to incorporate the following features:

(1) Thin vertical strips of the material should be submitted to an adjustable torque applied at the two ends, so that the stress should be uniform along the test-piece.

(2) The specimen should be immersed in a small vessel containing a stirred liquid, which could be maintained at any desired temperature.

(3) When under zero torsional load the specimen should be relieved of its own weight and that of the indicating and stressing mechanism.

(4) Provision should be made for measuring rate of flow under known stress, and recovery after subjection to either known stress or known strain.

The following is a description of an apparatus on these lines designed and made by one of the writers. In order to explain the technique of testing, it has been found necessary to describe a number of interesting results obtained with the apparatus, but the scientific and technical significance of these and other results will be discussed in a later report.

EXPERIMENTAL

1—Plastic Flow Apparatus

The torsion apparatus is illustrated in Figure A. The test-piece A is clamped at the lower end to the base B of the apparatus and at the upper end to a suspended clamp C. The weight of the specimen, clamp C and its attachments is supported by a weight D connected to the clamp by a fine thread passing over a pulley. This prevents the sample, when in a very plastic condition, from collapsing under the weight of the clamp. The supporting thread, since it lies along the axis of the specimen, exerts no torque. Consequently the weight D need not be accurately adjusted, it is quite unnecessary for example to take into account differences in density of the specimens or of the heating liquid.

A pointer E, which is rigidly connected to the clamp C, moves over a scale F fixed to the base by rods G which are adjustable in length to accommodate test-pieces of different lengths. The torque is applied to the clamp C by thin threads H which pass over freely suspended pulleys J and are wound round a vertical cylinder K fitted directly above and rigidly connected to the upper clamp. The cylinder device ensures that the torque applied is independent of deflection.

The apparatus is immersed in water, or, for temperatures above 100° C., in some liquid such as glycerol, to a sufficient depth to cover the upper clamp but not the scale. A 1500 cc. beaker is suitable for the purpose.

2—Experimental Procedure

For measurement of rate of flow under constant torque at any given temperature, the temperature of the liquid is adjusted to the required value before applying the torque, and when the pointer has ceased to move, due to shrinkage or warping of the test-piece or to recovery from previous strain, the zero reading is taken. At a noted time equal loads are applied to the threads and deflection-time readings are taken, the temperature being maintained constant. It is necessary to read both ends of the pointer and to take the mean in order to compensate for warp of the test-piece away from the vertical or for any eccentricity of the cylinder K with respect to the scales. The deflection can be read to

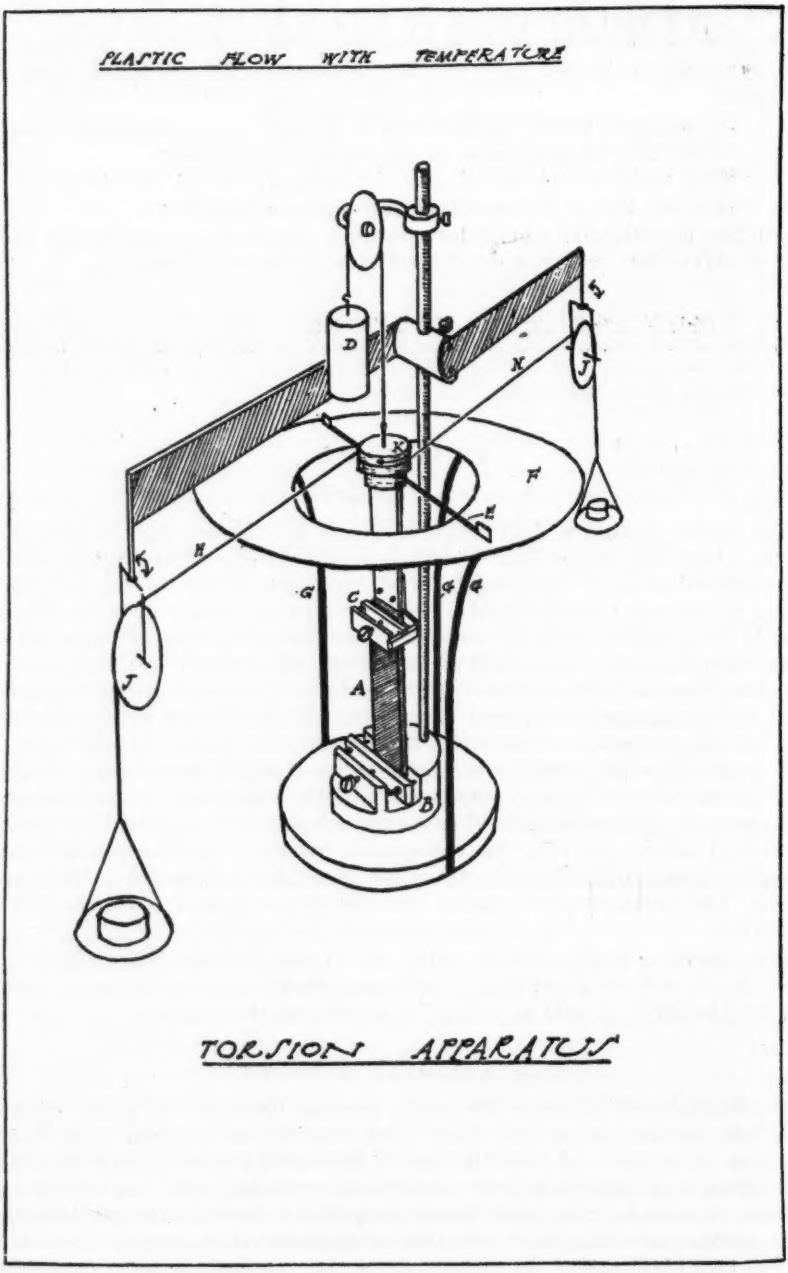
PLASTIC FLOW WITH TEMPERATURE
D
D
N
F
H
G
C
A
B
TORSION APPARATUS

FIG. A.

the nearest tenth of a degree of arc and is not usually permitted to exceed 10 degrees.

To measure rate of recovery after a definite time under constant torque, the loads are removed from the threads H and deflection-time readings are continued.

3—Influence of Some Experimental Conditions on the Plastic Deformation

(a) Relation between Deformation and Time at Various Temperatures.

In Figure B (1) are shown deflection-time curves up to about 30 minutes at various temperatures and under standard stress for a 65/35 rubber-sulfur mixing vulcanized for 5 hours at 60 lbs. per sq. in. steam pressure, the test-

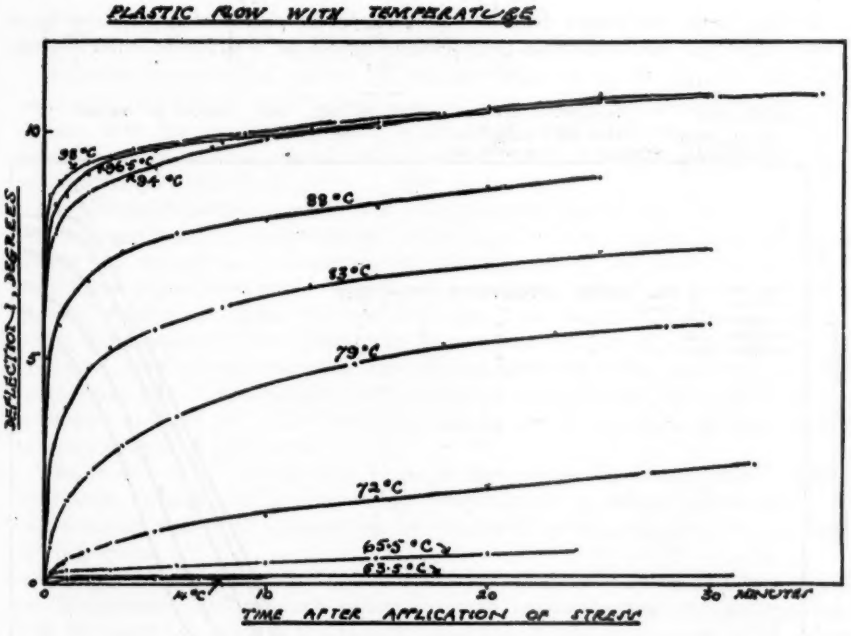

Fig. B (1).

pieces having the dimensions: length between grips 75 mm., width 19 mm. and thickness 5.5 mm.

The same test-piece was used for several curves, since it was found that with all the hard rubbers so far tested no error was incurred provided that the sample was allowed to recover its zero after each test and that the deflections were kept small. If tests are made at successively increasing temperatures, the deflection from the previous test is relatively small and the recovery is usually complete by the time the liquid bath has been raised to the next testing temperature. At the lower temperatures, where recovery is slower, it can be hastened by applying a small reverse stress for a short time and observing the pointer for a short time before applying the stress to ensure that there is no drift of zero.

Most of the curves show an initially rapid but continuously decreasing rate of flow with time, the curves appearing to approach an asymptote, and the rate of approach being greater the higher the temperature. Close approach to the asymptote takes considerably more than half an hour. For a similar material, deflection-time curves both at 68° C. and at 98° C. were extended up to 7 hours, but a constant deflection had not been reached after this time. Slow but noticeable drift was still taking place.

At low temperatures (53° C. and below) this type of flow cannot be detected, the hard rubber acting more nearly like a relatively rigid and purely elastic material; the asymptotic deflection is smaller and there is practically no drift after 1 or 2 minutes.

(*b*) *Relation between Temperature and Deformation after various Periods.*

In Fig. B (2) the above deflection-time curves at various temperatures have been converted into deflection-temperature curves at 5 different time periods

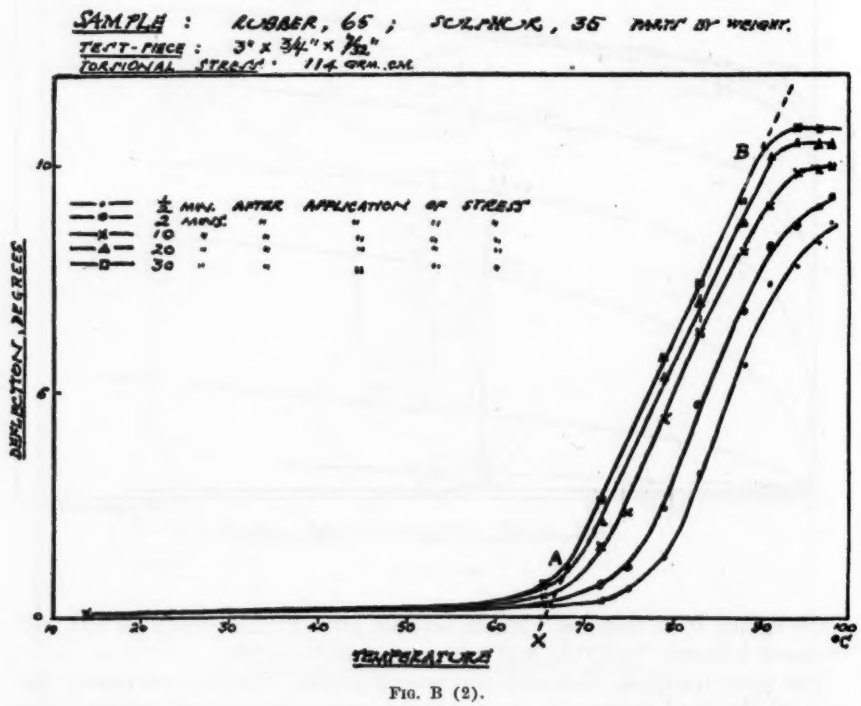
SAMPLE : RUBBER, 65 ; SULPHUR, 35 PARTS BY WEIGHT.
TEST-PIECE : 3" x 3/4" x 7/32"
TORSIONAL STRESS : 114 GRM. CM.
1/2 MIN. AFTER APPLICATION OF STRESS
2 MINS. " " " " "
10 " " " " "
20 " " " " "
30 " " " " "
DEFLECTION, DEGREES
TEMPERATURE
A
B
X
°C

Fig. B (2).

after application of stress. The temperature at which the relatively rigid and purely elastic condition changes to a condition of continuous flow is indicated by the point where the curves for different times commence to separate. It will be noticed that the rising portion of the curve is almost straight, particularly after relatively long times such as 20 and 30 minutes, and the knee of the curve occurs at a fairly definite temperature.

A convenient temperature for reference purposes is that indicated by the intercept of the rising straight portion of the 30 minute curve on the temperature

axis. A similar straight portion on the deflection-temperature curve is shown by all the hard rubbers so far tested, and the intercept temperature will therefore be defined as the "yield temperature" of the hard rubber sample. This is to some extent arbitrary, since it depends on the time interval selected, but after 30 minutes the initial rapid flow is passed, so that a difference of 10 minutes affects the yield temperature by only about 1° C. in the case shown in Fig. B (2). Moreover, the changes in deflection beyond 30 minutes are so slow that measurements made at this time give a good idea of the behavior of the material under prolonged stresses.

The deflection-temperature curves appear to approach a maximum deflection at high temperatures, as would be expected if the rigidity of the feeble "elastic phase" in the hard rubber, which is the main control in this region (see *J. Rubber Research* **5**, 20 (1936)) is comparatively independent of temperature.

(*c*) *Effect of Magnitude of Applied Stress.*

Deflection-temperature curves for various times up to 10 minutes and temperatures from 14° to 90° C. were obtained for a wide range of applied torsional stresses with the material and sample dimensions used in 3 (*a*) and (*b*) above. Where possible without considerably exceeding 10 degrees deflection, the torque was varied between about 100 and 4,000 g.-cm.

On plotting deflection against load it was observed that at all the temperatures and times stated the deflection was proportional to the applied torsional stress within the accuracy of measurement. The shapes of the deflection-time and deflection-temperature curves are therefore independent of the torsional stress applied, except of course that the deflection scale varies in proportion to the stress. Consequently, the yield temperature, as defined in paragraph 3 (*b*) above, is likewise independent of the applied torsional stress provided that the same stress is used throughout the temperature range or that the deflections are converted to those for a fixed stress by making use of the direct proportionality between deflection and stress.

This result is of considerable practical importance in testing hard rubber, since large stresses can be used at low temperatures to obtain high accuracy of measurement and small stresses can be employed at high temperatures to limit the deflections.

In many plastic materials there is a limiting stress or yield value below which no flow occurs. The proportionality observed between stress and deformation with the materials used in the present experiments implies that the yield value, if any, in the case of hard rubber is very small compared with the stresses involved in these tests.

(*d*) *Effect of Dimensions of Test-piece.*

The following standard dimensions for the test-piece used in the torsion apparatus have been adopted and will be employed wherever the size of the available material permits, but small variations in dimensions are unavoidable, particularly in thickness when the test-pieces are cut from moulded sheet: length of test-piece between clamps, 75 mm.; width, 15 mm.; thickness, 5 mm.

An empirical relationship between the dimensions of the test-piece and the deflection per unit torque was obtained by preparing a number of test-pieces in which each dimension was varied over a range of some $\pm 50\%$, the other two being maintained at constant values, and obtaining deflection-time and deflection-temperature curves in each case. A commercial unloaded hard rubber was used for these tests.

As was expected from the direct proportionality between load and deflection at all temperatures and times, the shapes of the deflection-time and deflection-temperature curves were independent of the dimensions of the test-piece except that the deflection scale of the curves varied. This is demonstrated in Table I where the 30 minutes intercept temperatures or "yield temperatures" for test-pieces of various dimensions are given. The temperatures are very closely the same in each case.

After it had been shown with these seven test-pieces that the shapes of the curves were constant except for variations in the deflection scale, several additional test-pieces of intermediate dimensions were prepared and tested at one temperature only (60° C.).

TABLE I

Sample No.	Approx. length (mm.)	Approx. width (mm.)	Approx. thickness (mm.)	Yield temperature (° C.)
1	100	18	5	46.0
2	75	18	5	46.0
3	50	18	5	45.5
4	75	25	5	46.0
5	75	12.5	5	45.5
6	75	18	7.5	45.5
7	75	18	2.5	46.5

From the results it was found that the relation between deflection per unit torque and dimensions is well represented by the following formula provided that the deviations from the standard size, $75\times15\times5$ mm., are not larger than about $\pm25\%$, though even larger variations in one dimension alone are permissible:

$$\text{deflection, } S=KT(D^{-\frac{1}{2}})(B^{-\frac{1}{2}})(L-L_0)$$

where D, B, and L are the thickness, width, and length, respectively.

T=the applied torque
L_0=a constant (=20 mm.)
K=a constant depending on the properties of the material under test, the testing temperature, and the time after application of the torsional stress.

Hence to reduce observed deflections to those for a standard test-piece under the same conditions of test, they must be multiplied by the factor

$$\left(\frac{B}{15}\right)^{\frac{1}{2}}\left(\frac{D}{5}\right)^{\frac{1}{2}}\frac{55}{L-20}$$ where B, D, and L are in mm.

4—Influence of Time of Vulcanization of Unloaded Hard Rubber

In order to demonstrate the importance of the test as an indication of the state of vulcanization of samples made from a mixing of known composition, the results of typical tests on an unloaded hard rubber vulcanized for a range of time periods will now be described.

A 68/32 rubber-sulfur mixing vulcanized for 3 different time-periods was submitted to this test. It was not possible to use test-pieces of standard length, but the following dimensions were employed: length, 45 mm., width, 15 mm., thickness, 5 mm. In Figure C deflection-temperature curves at three different times after application of stress are given. The curves represent the deflections uncorrected for deviation from the standard length of test-piece. The samples

made from the 68/32 rubber-sulfur mixing show the same general curve shapes as those made from the 65/35 mixing, shown in Figure B (2).

The effects of increasing vulcanization are (1) to raise the yield temperature probably to some limiting value; (2) to increase the slope of the middle linear portion of the deflection-temperature curve, and (3) to increase the rigidity of the material at the higher temperatures where the deflection becomes substantially independent of temperature, *i.e.*, above the middle straight part of the deflection-temperature curve.

A determination of a complete deflection-temperature curve is a lengthy proceeding, but it is unnecessary, for checking the state of vulcanization of samples made from a known mixing, to test more than the deformation after 30 minutes

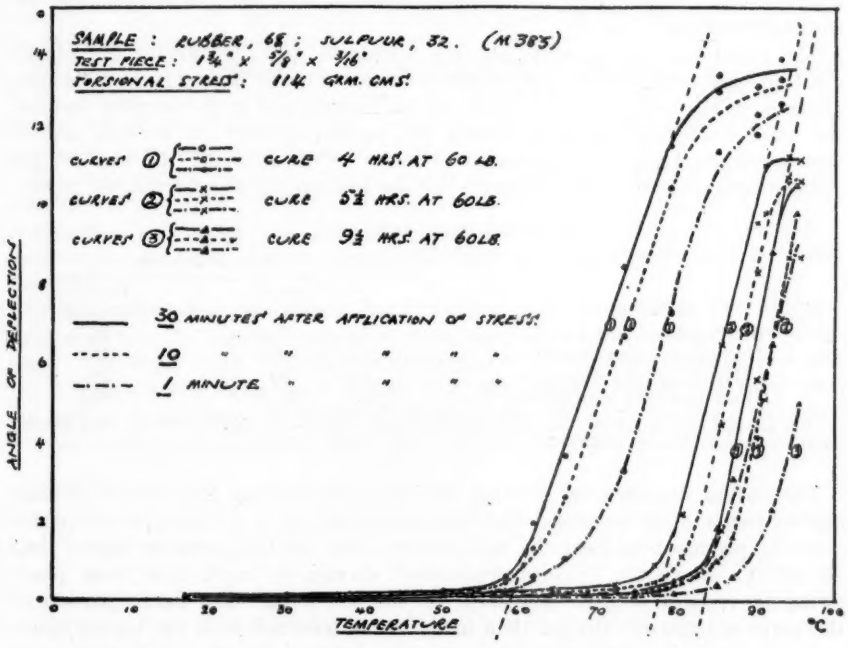
SAMPLE : RUBBER, 68 ; SULPHUR, 32. (M 383)
TEST PIECE : 1¾" × 5/8" × 3/16"
TORSIONAL STRESS : 114 GRM. CMS.
CURVES ① CURE 4 HRS. AT 60 LB.
CURVES ② CURE 5½ HRS. AT 60LB.
CURVES ③ CURE 9½ HRS. AT 60LB.
30 MINUTES AFTER APPLICATION OF STRESS.
10 " " " " "
1 MINUTE " " " " "
ANGLE OF DEFLECTION
TEMPERATURE
°C

FIG. C.—Plastic flow with temperature effect of cure on hard rubber.

at a single temperature. It is clearly necessary to select the temperature of test carefully to avoid the flat portions of the curve above and below the central straight portion.

The curves for samples made from mixing M383 (cf. *J. Rubber Research* **5**, 15 (1936)) connecting temperature with set after constant torsional strain, were obtained with the same material as was used in the present investigation, and it is noteworthy that the temperature of maximum set in Figure 2 increases with advancing vulcanization in the same way as the yield temperature in Figure C.

5—SUB-PERMANENT SET

After the materials used in tests described in Section 4 had been stressed for 30 minutes, the torque was removed and the recovery observed during a further

period of 30 minutes. Sub-permanent set at the end of this period, expressed as a percentage of the full deflection after 30 minutes under load and plotted against temperature, gave curves having maxima at the same temperatures as before (cf. *J. Rubber Research* **5**, 15 (1936)). The recovery curves are not given here, since this question has been discussed fully (*J. Rubber Research* **5**, 11 (1936)).

6—Comparison with Martens Apparatus

Deflection-time curves were obtained with the Martens apparatus at a range of steady temperatures on an unloaded hard rubber prepared in the laboratory and on three commercial products. All samples, with the exception of the first mentioned, were of the Martens standard dimensions. The laboratory-prepared material was thinner, and the bending moment used on the sample was accordingly reduced.

The apparatus was placed in an air-oven for the test, and during the adjustment of the temperature the weight was not allowed to exert any bending moment on the test-piece. To eliminate the uncertainty as to the zero position, the amount of flow occurring during the period between 30 seconds and 30 minutes under stress was measured. Great care in applying the load at the commencemnet of test was necessary for the attainment of reproducible results.

Table II

Hard rubber	Yield temperature, ° C. Martens apparatus	Torsion apparatus
65/35 rubber/sulfur	69.5	68
Unloaded commercial	46.5	45
B.E.S.A. grade, unloaded	60	59
Heat resistant red quality *	90–91	84.5

* The samples used in the two tests were supplied independently and may therefore be from different sheets of slightly different properties.

The curves obtained on plotting the total flow during this period of time against temperature possessed the same characteristic of a linear portion which could be produced to meet the temperature axis. At temperatures higher than 10°-15° C. above the "yield temperature" excessively rapid yield took place, owing to vertical collapse and shear of the test-piece. The linear portion of the curve is relatively steeper than in the curve obtained with the torsion apparatus for the deflection during the same time interval (30 sec. to 30 min.), and this is considered to be due to the instability of the system, leading to vertical collapse of the specimen under the weight of the loading device. The curvature of the test-piece after the experiment was not symmetrical, indicating that a pure four-point stress is not applied by this method of loading, at least at high temperatures.

The intercept temperature or "yield temperature" is given for each of the materials tested in Table II, where a comparison with the corresponding figure obtained with the torsion apparatus is made.

It is apparent from the results that the Martens apparatus, used in the manner described above and not as in the V.D.E. test, gives a slightly higher value for the yield temperature than the torsion apparatus, but the difference is in general not large. It seems therefore that flow under torsional stress depends on essentially the same properties of the material as flow under bending stress.

It is considered that for convenience of operation and completeness of the data obtainable the torsion apparatus is to be preferred for the present investigation on hard rubber.

SUMMARY

The merits of the Martens apparatus as an instrument for measuring plastic flow of solid insulating materials at various temperatures are discussed and the features of a new torsion apparatus which is designed to overcome certain objections to the Martens apparatus are explained. Details of the construction of the new apparatus and of its method of operation are given.

Deflection-time and deflection-temperature curves determined with the torsion apparatus for a typical hard rubber are given and the form of these curves is discussed. The "yield temperature" is defined from the characteristic shape of the deflection-temperature curve.

It is shown that deflection is proportional to stress, and that the magnitude of the stress used and the dimensions of the test-piece have no influence on the general shape of these curves. An empirical formula connecting deflections, stress and test-piece dimensions is given.

The influence of degree of vulcanization on the plastic flow of an unloaded (rubber-sulfur) hard rubber at various temperatures is described. "Yield temperature" increases with time of vulcanization up to some limiting value. Recovery of shape of the test-piece after removal of torsional stress is briefly discussed.

Comparative tests on several hard rubbers were made with the Martens apparatus and the torsion apparatus, both used at a series of steady temperatures. The same type of deflection-temperature curve was obtained, but the "yield temperature" as slightly higher with the Martens apparatus than with the torsion apparatus. The torsion apparatus provides more complete data and is more convenient to operate than the Martens apparatus.

FROSTING OF VULCANIZED RUBBER *

W. F. TULEY

NAUGATUCK CHEMICAL, DIVISION OF UNITED STATES RUBBER COMPANY, NAUGATUCK, CONN.

Rubber products, like most commodities today, must meet the public demand for attractive appearance. Anything which damages the finish is a problem for the technical man. An appearance problem which seems to have become frequent in recent years is concerned with a dulling or surface dimming of various types of rubber goods after vulcanization. This effect has been aptly called "frosting," and it sometimes resembles actual frost.

Frosting may be easily confused with bloom. It usually appears within a few hours or days after vulcanization. It differs from bloom in that it is not caused by migration to the surface of a component of the rubber composition. Bloom can usually be removed by solution in weak acid or alkali or in an organic solvent. Frosting cannot be removed. The microscopic appearance is also quite different.

Frosting may occur on rubber vulcanized in a press or in an open-air or steam cure, such as is used for footwear. It is most noticeable on the bright finish of air-cured rubber goods. Sometimes it appears almost immediately after removal from the vulcanizer as a bluish sheen, which may later become almost gray. Frosting has been observed on a great variety of rubber products, including footwear, raincoats, inner tubes, druggist's sundries and other molded articles. Unfortunately there is no known way in which frosting can be removed after it has once formed. It can be covered with lacquer or other finish but this is seldom satisfactory when applied after vulcanization. A bloom of sulfur and sometimes of other materials can be removed by additional heating at vulcanizing temperatures, but this is not effective with frosting. If the rubber is not frosted within a few weeks after vulcanization, it seems to develop a resistance to frosting and is unlikely to frost later.

Frosting was determined to be due to the ozone in the air. So far as the writer knows, the cause was first determined by S. M. Boyd in 1931. He found that the effect could be reproduced by exposing vulcanized rubber without tension in warm, humid, ozonized air.

FROSTING TEST

A simple and rapid determination of the relative tendencies of different stocks to frost may be made by means of this test:

The equipment shown in Figure 1 consists of a chamber, roughly 2 feet on each side, which is provided with an ozone generator for producing ozonized air. Suitable ozone generators may be purchased from manufacturers of this equipment or may be made by a design recently described[5]. A moderate stream of dry air is passed through the ozone generator during the operation to ensure maximum efficiency. The ozonizer operates on the 110-volt a. c. lighting circuit. A 100-watt light bulb serves to heat the interior of the box.

In making the test, a sheet of blotting paper is saturated with water, laid flat on a glass plate placed in the box with the generator and light operating,

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and left for about one hour. The box should be tightly closed. The blotter is then thoroughly wet again, and the rubber samples to be tested are placed upon it. Care is taken that there is no water on the surface to be frosted. Under these conditions frosting is quite rapid. The time of exposure varies from a few minutes up to 3 hours, depending on the nature of the stocks and on the degree of frosting desired. Measurements show a temperature of 127° to 130° F. and a relative humidity of 70 to 75 per cent while the box is operating as described. Lowering the temperature and humidity slows the test and, if there is insufficient humidity, frosing will not take place.

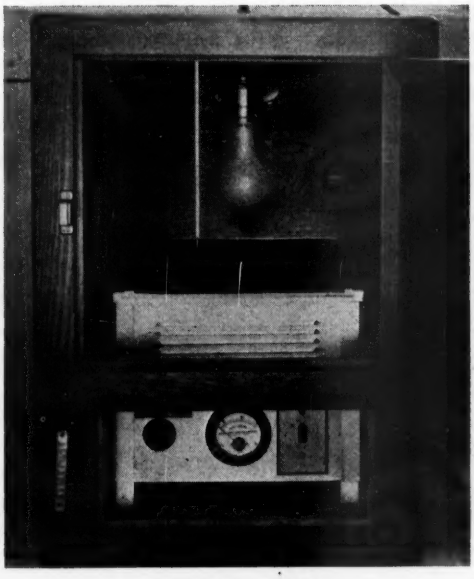

FIG. 1.—Frosting test apparatus.

REACTION OF OZONE AND RUBBER

Frosting occurs almost exclusively in warm, humid weather. Apparently the activity of the ozone or the rubber is increased by moisture and warmer temperatures. Also under such weather conditions, windows are open and the outside air circulates a great deal more indoors than at other seasons.

Air is known to contain a minute amount of ozone, estimated by Reynolds[4] at 5 to 12 volumes per billion volumes of air. It is supposed to be formed in the upper atmosphere by ultraviolet light and reaches the lower atmosphere by diffusion and convection currents. The concentration is undoubtedly variable and tends to a maximum in the spring. An attempt was made to determine atmospheric ozone by the best chemical methods described[1] and with all possible precautions. The maximum amount found was 1.9×10^{-7} gram per liter of air, or about 0.10 p. p. m. by volume of air. This determination was made in June and July, 1936.

Ozone was first shown by Williams[8] in 1926 to be the cause of the cracking of rubber under tension. This was further established by van Rossem[7], who proposed the term "atmospheric cracking" to describe this effect.

Ozone attacks the double bonds of rubber to form an ozonide[3]. The primary or secondary reaction product of ozone on rubber is a viscous liquid lacking in physical strength and therefore unable to withstand a stress. It appears that where ozone attacks stretched rubber it breaks and thus relieves the tension in adjacent areas and decreases its reactivity to ozone. The strain is increased in the crack, and ozone continues to react at that point and cause the crack to grow. The surface strains in a piece of rubber are undoubtedly very nonuniform and result in a nonuniform reactivity ozone.

It is not generally recognized that ozone will react with rubber which is not under tension. H. L. Fisher found that a sample of unstressed pure gum stock in ozonized oxygen gained 0.2 per cent of its weight in 6 hours at room temperature. After the final weighing it was bent but showed no cracks, even under microscopic examination. Fisher also found that vulcanized rubber swollen by benzene cracked in ozonized oxygen; the strain produced by solvent absorption

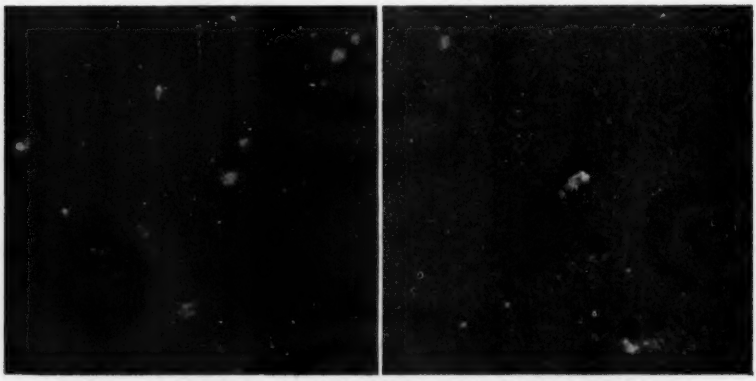

FIG. 2.—Unfrosted (*left*) and frosted (*right*) rubber surfaces (×70).

evidently had the same effect as tension. The action of ozone is not restricted to soft vulcanized rubber. Fisher found that bent samples of hard rubber, 0.5 mm. thick with a coefficient of vulcanization of 43, cracked in less than 2 minutes in ozonized oxygen.

OZONE CRACKING AND FROSTING

Rubber behaves like a supercooled liquid with colloidal properties. Liquids exhibit surface tension, and this property is retained in supercooled liquids and solids[6], although it is not so easily demonstrated in the latter. Evidence of the surface tension of rubber is that the surface of unvulcanized rubber flows when its viscosity is reduced by heating. This seems to explain the glossy finish on air-cured rubber.

The surface of rubber is therefore under tension, even though the mass of the rubber is not strained. The surface is thus reactive to ozone. When exposed to ozonized air, the surface is disintegrated into a maze of minute cracks. This microscopically cracked surface designated as frosting is distinguished from atmospheric cracking of stretched rubber principally in the size and number of the cracks.

The surface of vulcanized compounded rubber is essentially a continuous transparent film of rubber which transmits or reflects light without diffusion. The appearance and color of a pigmented rubber composition depend on the selective absorption and reflection of light by the pigment dispersed in the rubber. Disintegration of the surface rubber film causes it to reflect diffused light directly, and the color of the underlying pigment is obscured.

Figure 2 (left) shows a photomicrograph of the surface of a glossy black rubber compound. The clear blackness results from the absorption of light by the black pigment under the continuous, transparent rubber surface. The same surface is shown at the right after it has been frosted. The granular appearance is due to the reflected light from the disintegrated and cracked surface. The larger objects on the surface are dust or pigment particles picked up during handling.

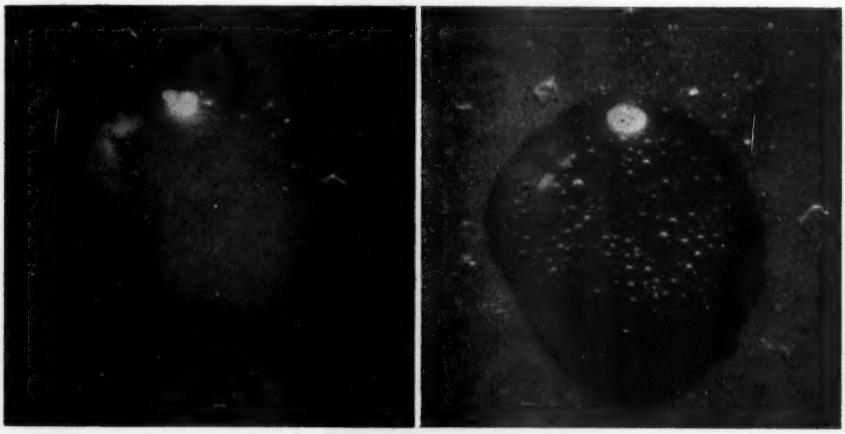

FIG. 3.—A drop of dilute hydrochloric acid on (*left*) an unfrosted and (*right*) a frosted rubber surface containing whiting.

In severe frosting the ozone disintegration of the surface exposes some filler particles which further interfere with the transmission of light and increase light diffusion. If a frosted rubber stock contains whiting, it can easily be demonstrated that the pigment particles are exposed by treating with dilute acid and observing the evolution of carbon dioxide. Zinc and other elements extractable by aqueous acids can be detected in an acid extract of the frosted surface. In an unfrosted or bloomed surface, the pigment particles are coated by a film of rubber and are not so easily attacked by dilute acids. Extraction of a pigment from a frosted surface does not restore the original appearance.

Figure 3 (left) shows a drop of dilute hydrochloric acid on an unfrosted surface. At the right a similar drop of acid is shown on the same rubber sample after frosting. This rubber compound contained whiting and the gas bubbles visible in the drop of acid are carbon dioxide being evolved from the frosted surface. The acid is prevented from reacting with the pigment in the unfrosted sample by the continuous rubber surface.

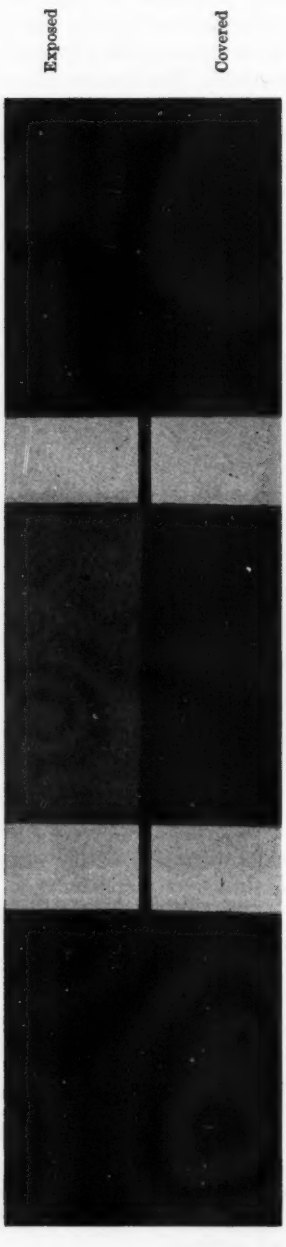
Exposed
Covered
0.35 part of 4,4'-diaminodiphenylmethane per 100 parts of rubber.
Air-cured rubber control, no protective agent.
0.50 part of antifrosting wax per 100 parts of rubber.

FIG. 4.—Effect of antifrosting chemicals.

PREVENTION OF FROSTING

Rubber vulcanized with aldehydeamine accelerators seems to be more resistant to frosting than rubber vulcanized with thiazoles, dithiocarbamates and guanidines, which are now more widely used. It is believed that frosting was not encountered until recent years because the accelerators formerly used produced vulcanized rubber less sensitive to ozone than that obtained with the present accelerators.

Obviously frosting can be prevented by any protective film which excludes ozone from contact with the rubber. Varnished and lacquered surfaces do not frost. Also chemical treatments which reduce the chemical reactivity of the surface will reduce its tendency to frost. Treatments with chlorine, bromine or sulfur monochloride are effective.

Frosting is also inhibited by incorporating a small proportion of certain high-melting special petroleum waxes which bloom to the surface and form a protective film. Casper wax[2] from a Wyoming petroleum field is most effective. Ordinary paraffin is without effect. Excessive wax bloom may affect the adhesive qualities of the unvulcanized rubber or the finish after vulcanization. One-half per cent of wax on the rubber can generally be used without a noticeable bloom, but this is not sufficient to give complete protection against frosting and atmospheric cracking.

A large number of chemical have been investigated for inhibiting frosting by the laboratory frosting test. It is noteworthy that the chemicals which have been found to inhibit frosting in the laboratory accelerated test have confirmed this result under natural frosting conditions. Some aldehydeamine and ketone-amine antioxidants are sometimes slightly effective in inhibiting frosting. Most of the usual types of antioxidants and antiflex-cracking agents are entirely without effect. A limited number of chemicals have been found which are of any value. The most effective of these are all members of one class, the diprimary aryl amines, represented by *p*-phenylenediamine, benzidine-(4,4′-diaminodiphenyl)- and 4,4′-diaminodiphenylmethane.

p-Phenylenediamine and benzidine are toxic chemicals unsatisfactory for commercial use. 4,4′-Diaminodiphenylmethane has some antioxidant properties, and gives some activation of the cure, for which allowance should be made. It has been in commercial use for a number of years and is far superior to other known antifrosting chemicals.

The effect of these antifrosting agents is shown in Figure 4. These samples were subjected at the same time to ozonized air in the frosting chamber, with the lower half of each sample covered with tinfoil. The protective action of the added chemicals is clearly demonstrated.

This discussion of frosting should not be completed without emphasizing that it is only one of the causes for objectionable changes in the finish of vulcanized rubber products, but it should be suspected in any case not obviously of another type.

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OIL-RESISTING RUBBER

PART XII. VULCANIZED RUBBERS CONTAINING ORGANIC ACCELERATORS *

J. R. Scott

I. INTRODUCTION

In spite of the vast amount of work which has been devoted to organic accelerators and their influence on the physical properties of the vulcanizate, very little information can be found in the literature concerning their influence on the swelling of the vulcanizate in organic liquids.

The present experiments were not intended to form a systematic investigation of the influence of organic accelerators on the swelling properties of the vulcanizate, but rather to obtain a general idea of the swelling of rubbers containing the commoner types of commercial accelerators and to find out to what extent swelling could be correlated with the mechanical properties and combined sulfur content of the vulcanizate.

II. EXPERIMENTAL

The mixings examined consisted in each case of rubber 100, zinc oxide 3, plus sulfur and accelerator as shown in Table I, which gives also the vulcanization temperature and optimum vulcanization time. The details of preparation and the mechanical properties of these rubbers, from which the optimum vulcanization times were deduced, have been tabulated and fully discussed elsewhere (Dawson[7]). Swelling was measured by immersing a disc of the rubber (16 mm. diameter, 5 mm. thick) in benzene for 100 hours at 25° C. As the number of samples was very large and the work was only of a preliminary nature, the complete time-swelling curve was not examined; consequently the swelling maximum (for definition *see* Scott[5]), which is the true measure of swelling capacity, could not be determined. Under the experimental conditions used, however, the swelling after 100 hours was sufficiently close to the swelling maximum for the purposes of the present investigation.

The detailed results are given in Table II, and the swelling for each mixing at its optimum vulcanization and at $\frac{3}{4}$ of this vulcanization time, *i.e.*, approximately a technical vulcanization, is shown in Table 1, together with the vulcanization coefficient at optimum vulcanization. All swelling results represent the volume of absorbed liquid expressed as a percentage of the volume of the rubber.

III. SUMMARY AND CONCLUSIONS

(1) Addition of an organic accelerator to a rubber mixing may modify the swelling capacity of the vulcanizate in one or more of three ways: (*a*) by altering the vulcanization coefficient; (*b*) by shortening the time of vulcanization and/or lowering the requisite vulcanization temperature, thus lessening depolymerization and reducing the swelling; (*c*) by exerting a direct effect on the rigidity of the rubber, independent of (*a*) and (*b*); in some cases at least this direct effect of the accelerator renders the rubber stiffer and reduces the

* Condensed from the *Journal of Rubber Research*, Vol. 8, No. 2, pages 11-19, February 1939.

swelling; this effect is so pronounced that the swelling of an accelerated rubber cannot be deduced solely from its combined sulfur content and the time and temperature of vulcanization.

(2) With the exception of rubbers too undervulcanized to be of technical importance, there is an approximate proportionality between swelling, elongation at 0.5 kg. per sq. mm. and plastometer-hardness number. Apart from actual swelling tests the hardness is probably the best guide to the swelling capacity of a rubber, because the swelling/hardness relationship is not greatly affected by the commoner inorganic compounding materials; elongation at constant load is less satisfactory because its relationship to swelling is affected by these ma-

TABLE I

Mix No.	Sulfur	Accelerator	Optimum vulcanization Temp. °C.	Optimum vulcanization Time min.	Swelling Opt.	Swelling ¾ opt.	Vulcanization coefficient opt.
1	5	1 Aldehydeammonia	153	30	411	432	3.19
2	5	1 Hexamethylenetetramine	153	50	360	380	3.44
3	5	1 Thiocarbanilide	153	80	485	530	3.0
4	3	1 Triphenylguanidine	141	105	568	640	1.34
5	3	1 Diphenylguanidine	141	95	388	402	2.24
6	3	½ Di-*o*-tolylguanidine	141	80	394	418	2.15
7	5	3 Lead dimethyldithiocarbamate	138	40	472	491	1.80
8	3	2 Piperidine pentamethylenedithiocarbamate	126	65	390	435	2.08
9	3	¼ Piperidine pentamethylenedithiocarbamate	126	40	438	443	1.52
10	2	¼ Tetramethylthiuram disulfide	126	20	419	437	1.63
11	2	¼ Tetraethylthiuram disulfide	126	25	400	430	1.70
12	5	¾ Ethylideneaniline	141	50	403	426	2.09
13	5	½ Quinoidine	141	90	515	556	1.93
14	5	2 Anhydroformaldehyde-*p*-toluidine	141	65	358	420	2.12
15	5	4 Formaniline	141	65	382	482	1.94
16	5	4 Methylene dianilide	141	65	365	454	2.08
17	5	1 Proprietary accelerator, mainly ethylideneaniline	141	60	366	379	2.69
18	3	½ Ethylideneaniline	141	75	446	471	1.77
19	3	½ Diphenylguanidine + ⅛ ethylideneaniline	141	75	419	440	1.6
20	3	⅔ Diphenylguanidine + ⅓ anhydroformaldehyde-*p*-toluidine	141	75	409	443	1.7
21	3	⅔ Diphenylguanidine + ⅓ formaniline	141	90	404	454	1.83
22	3	⅔ Diphenylguanidine + ⅓ methylene dianilide	141	75	406	438	1.75

terials. Bridgwater's statement as to the absence of a relationship between swelling and stress-strain properties (*see* Introduction) is incorrect when swelling is taken to mean the maximum liquid-absorbing capacity.

(3) One of the main problems involved in making an oil-resisting rubber is that of reducing swelling without reducing deformability, since the rubber must possess the latter in a certain predetermined degree. As the accelerated rubbers are found to have practically the same ratio between swelling and deformability as unaccelerated rubbers, the present experiments provide no evidence to show that the use of organic accelerators will help to solve this problem. Bridgwater's statement that oil-resisting rubbers should be highly accelerated is probably based on his observations that at a given "physical

state of cure" *i.e.*, position of stress-strain curve, the initial rate of swelling is lower the more rapid the vulcanization (this, of course, does not apply to the swelling maximum). For rubbers which are in contact with swelling liquids for intermittent short periods, the use of accelerators therefore appears to be advantageous.

TABLE II

Mix No.	Time of vulcanization (min.)	Swelling	Mix No.	Time of vulcanization (min.)	Swelling	Mix No.	Time of vulcanization (min.)	Swelling
1	20	431	9	30	441	16	20	791
	30	411		40	438		35	500
	40	437		50	435		50	423
							65	365
2	20	468	10	10	468		80	344
	35	375		20	419		95	332
	50	360		30	421			
	65	375				17	30	399
			11	10	915		40	379
3	65	505		20	407		50	370
	80	484		30	397		60	366
	95	477		40	431		70	368
				50	452		80	371
4	20	1581		60	465			
	35	923						
	50	747						
	65	661	12	30	434	18	30	518
	85	592		40	412		45	483
	105	568		50	403		60	456
				60	399		75	446
5	20	587					90	444
	35	471	13	30	775		105	445
	50	423		45	620			
	65	399		60	557			
	80	391		75	515	19	60	429
	95	388		90	498		75	419
				105	490		90	413
6	20	602						
	35	480	14	20	757			
	50	424		35	457	20	60	426
	65	403		50	396		75	409
	80	394		65	358		90	399
	95	390		80	335			
				95	326			
7	20	500				21	60	454
	30	488					75	419
	40	472	15	20	1000		90	404
	50	468		35	542			
				50	445			
8	50	415		65	382	22	60	420
	65	390		80	357		75	406
	80	387		95	331		90	400

(4) Swelling varies greatly with the state of vulcanization, the variation being similar in nature and magnitude to that observed in the case of elongation under a constant load or plastometer-hardness number (see Table II). Bridgwater's observation that swelling does not change much with cure is true only of the initial rate of absorption.

FATIGUE IN RUBBER

PART III. FATIGUE AND REINFORCEMENT *

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Rubber, unvulcanized and vulcanized, is both elastic and plastic and it is generally accepted that the function of vulcanization is to decrease the plasticity rather than to develop elasticity. It is, of course, essential that unvulcanized rubber after mastication should be predominantly plastic to allow all of the usual factory processing of the unvulcanized material. Incidentally it should be mentioned that this is one of the most difficult problems connected with the synthesis of artificial rubbers, namely, to produce a rubber which is essentially plastic before vulcanization and yet predominantly elastic after vulcanization. From the point of view of theoretical conceptions, various theories have been put forward to explain the elasticity of rubber. The old mechanical analogies of elastic bags containing fluid are of historical interest only.

The first theory, which was attractive in many respects, was the spiral molecule theory of Meyer and Mark, but it has since been generally recognized that it is not in agreement with many of the known facts, and the theory has been dropped.

Then came the hydrogen-evaporation theory of Mack, and here again it was not in conformity with some of the experimental facts about the elasticity of rubber. The present generally accepted view is that rubber elasticity is due to the thermal energy of long chain molecules which are, at ordinary temperatures, neither crystalline nor of such internal viscosity as to make internal movement difficult, *i.e.*, when aligned by stretching the molecules are held in position by internal forces. The rubber molecule is so long that from the point of view of its length it should be visible under the microscope, but its extreme thinness still makes resolution impossible. In other words, it is the physical approach to the geometrical definition of a line. The stretching of rubber consists of the alignment of these long threads and retraction consists of the long threads rearranging themselves in the position of normal disarrangement, due to the thermal motion. It is important, however, to realize that the long chain condition is not sufficient of itself for elasticity as, for example, in gutta, where long chains are present, but are already in the form of crystal aggregates at ordinary temperatures. Comparative freedom of movement of the chains must also exist to allow the thermal motion to cause disarrangement of the aligned threads in a short time. This gives rise to what the rubber technologist calls "snap." It must not be supposed, however, that lack of "snap" necessarily gives rise to high permanent set, as certain long chain vinyl resins are known which do not possess "snap," but which return slowly after stretching to almost exactly their original length. This time factor is controlled partly by the modulus of the material but mainly by the viscosity of the material. In gutta, for example, the internal forces at ordinary temperatures are such that there is some orderly arrangement of the long molecules, with the result that the material is practically

* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 14, No. 6, pages 340-360, April 1939.

non-elastic, but if warmed to higher temperatures free movement of the molecules becomes possible and the material begins to exhibit elastic characteristics. In the same way rubber at lower temperatures becomes non-elastic and can be "cold-drawn," *i.e.*, the molecules can be aligned without recovery like guta. When rubber is vulcanized the long chains are stitched together with sulfur bridges with the result that elasticity is still possible up to the stage of vulcanization, when a complete stitching of the chain has made rearrangement impossible (ebonite). On the other hand, stitching has made more difficult the formation of aligned aggregates which are probably the cause of plasticity in uncured rubber.

Rubber should, therefore, be defined as a state of matter rather than as a definite chemical individual. The conclusion is that the synthetic rubbers of the distant future may even be perfectly stable long chain inorganic products and in no way connected with the chemical constitution of natural rubber. Perhaps one of the most striking definitions of the rubber state is that given by Meyer[1], namely, that the rubber is a substance which is liquid in two directions and solid in the third. It should also be kept in mind that internal viscosity is not only subject to temperature but also to physical condition such as compression or extension.

Turning now to the stress-strain curve of rubber, one can easily understand the significance of the three regions. Region A corresponds to true rubber elasticity where the internal viscosity is low enough for the thermal motion to take effect. Region B is where fibre development takes place or crystallization in one direction shown by the Gough-Joule effect and also plastic flow of the fibres. Region C is approaching the true solid state of complete crystallization. As the molecule changes into the so-called crystalline condition, the properties of rubber change correspondingly towards the properties of ordinary solid bodies and the elastictiy becomes the elasticity of solid bodies, namely, produced by distortion of the crystal lattice. Crystallization of rubber can be brought about in various ways, *e.g.*, by freezing, or by simple stretching to a certain minimum value or by the application of smaller stresses for long periods of time, and possibly by repeated small stresses over a long period of time. The only evidence there is for this last type of crystallization is from knowledge of metal fatigue failure under rapidly alternating stresses. Although the complete explanation of this phenomenon is not yet known, in general it is thought to be associated with further crystallization of the material due to the continued application of stress, followed by a consequent tendency to brittleness. In particular, high frequency stresses cause fractures in metal samples with loads well below the elastic limit defined by Hooke's law. A probable explanation of this effect is that in static measurements, full recovery is possible after removal of the load as the time necessary for recovery is relatively short, but with high-speed stressing irreversible changes set in due to the impossibility of complete recovery before renewal of the stress. Knowledge of materials can thus be extended by comparison with experience in other fields, and fatigue, cold flow, strain hardening, etc., have a definite place in both metal and rubber technology (see Table I).

The physical degeneration of rubber under repeated stresses such as the well-known phenomenon of flex-cracking is undoubtedly brought about by at least two effects: (1) deterioration of the rubber due to oxidation brought about by the heat produced by the flexing, and (2) true fatigue connected with the actual crystalline structure of the rubber.

(1) *Chemical Deterioration.*—The development of heat is produced chiefly by the friction of the gas black particles together with the friction of the rubber

molecules in changing from the haphazard arrangement into the aligned arrangement and *vice versa*. Comparative experiments conducted with synthetic rubbers, which possess far better resistance to oxidation than natural rubber and inferior elastic properties, yield products with better resistance to flex-cracking, a fact which points to the importance of the oxidation factor in the flex-cracking of rubber.

(2) *True Mechanical Deterioration.*—This is connected with the behavior of crystallized or "solid" rubber. Little is known about this effect, as it is masked by oxidation changes. However, it has been shown that fatigue results in structural changes, as evidenced by power loss measurements and determinations of modulus in two directions at right angles. Havenhill[2], using the St. Joe flexometer showed that a certain anisotropy develops on fatigue at 800 revolutions per minute. Also changes in modulus on fatigue were demonstrated in Part II[3].

TABLE I

Liquid	Transition types	Solid
	Liquid crystals, glasses, rubbers, resins, metal aggregates.	Single crystals, *e.g.*, quartz.
Complete molecular disorder.	Intermediate state of disorder.	Complete molecular arrangement.
Viscous material.	Visco elastic, elasto-viscous materials.	Elastic material.
Complete recovery from molecular displacements.	Incomplete recovery from stress, particularly in alternating fields.	Complete recovery from displacements even in H. F. fields.
No structural effects.	Racking, permanent set, creep, strain hardening, fatigue phenomena.	Cleavages and brittleness.
No tensile strength.	Intermediate tensile strength.	Nearly theoretical tensile strength.

FATIGUE TESTING

An examination of the various flexing and fatigue tests reveals two essentially different types, which correspond to two different service conditions. The two conditions are called constant-load flexing and constant-deformation flexing, respectively. The loads and deformations are alternating and dynamic in character and have nothing to do with the static load, which simply determines the operating point on the stress-strain curve. Constant load flexing is best seen in a tire tread and constant deformation flexing in belts. Intermediate types of flexing, which may be called constant energy flexing, no doubt occur in some parts of a tire. The apparatus to be described in this paper can be used for either type of flexing, but is not intended without modification for destructive tests.

Now the two extreme types of flexing conditions lead to different heat developments in a series of compounds of different modulus and resilience.

The heat developed per cycle in constant load flexing is $\frac{1}{2}.\frac{(100\text{-}R)W^2}{100S}$ energy units where W is the load, S the dynamic stiffness, and R the resilience per cent, in constant deformation flexing equals $\frac{1}{2}.\frac{(100\text{-}R)SX^2}{100}$ energy units where X is the dynamic displacement. The dynamic stiffness comes into the

denominator of the first expression and the numerator of the second, a fact which will lead to a very different rate of heat production and resulting chemical deterioration.

As an illustration of the importance of this point, if by some method the resilience be increased and modulus decreased, as in the Firestone patent on black flocculation, it will have little effect on heat production in tread type flexing but a great lowering of heat production in belt type flexing. Hence, such a patent is of significance for sidewalls and belts and not for treads, from a heat standpoint. Conversely, if one can improve resilience without altering modulus, a great reduction of heat produced in tread flexing will result for this type of deformation. This can now be achieved by the use of a special

TABLE II

Rubber	Zinc oxide	Paraffin wax	Stearic acid	Kosmos T	Lamp black (Magecol)	P-33	Shawinigan	Whiting	Devolite	Sulfur	Mercaptobenzothiazole
100	5	—	4	20	—	—	—	—	—	3	0.625
100	5	—	4	30	—	—	—	—	—	3	0.7
100	5	—	4	40	—	—	—	—	—	3	0.75
100	5	—	4	50	—	—	—	—	—	3	0.85
100	5	—	4	60	—	—	—	—	—	3	1.0
100	5	—	4	—	—	—	30	—	—	3	0.75
100	5	—	4	—	—	—	40	—	—	3	0.75
100	5	—	4	—	—	—	50	—	—	3	0.75
100	5	—	4	—	30	—	—	—	—	3	0.75
100	5	—	4	—	40	—	—	—	—	3	0.75
100	5	—	4	—	50	—	—	—	—	3	0.75
100	5	—	4	—	—	30	—	—	—	3	0.75
100	5	—	4	—	—	40	—	—	—	3	0.75
100	5	—	4	—	—	50	—	—	—	3	0.75
All the above samples were cured for 45 minutes at 141° C.											
100	5	2	1	—	—	—	—	100	—	2.5	1.0
100	5	2	1	—	—	—	—	200	—	2.5	1.0
100	5	2	1	—	—	—	—	300	—	2.5	1.0
100	5	2	1	—	—	—	—	—	100	2.5	1.0
100	5	2	1	—	—	—	—	—	200	2.5	1.125
100	5	2	1	—	—	—	—	—	300	2.5	1.25
100	50	—	1	—	—	—	—	—	—	2.5	0.5
100	100	—	1	—	—	—	—	—	—	2.5	0.5
100	150	—	1	—	—	—	—	—	—	2.5	0.5
All the above samples were cured for 30 minutes at 141° C.											

black described later in this paper. It would, therefore, appear that it is not possible to design one rubber compound to give the best effects in all parts of the type from the point of view of heat development on flexing.

With these reservations in mind, an investigation was carried out on a number of very simple compounds, given in Table II, on the Vogt fatigue flexing machine which is of the constant deformation tire, with a view to correlating fatigue life with heat development.

Figure 1 shows the life in minutes on this machine against Shore hardness. It will be seen that the curves fall into three main categories. The figures in brackets give the range of tensile strengths for the three groups. The fillers used can be classified as reinforcing, diluent or weakening, according to their effect on tensile strength.

The following general equation, which is of an empirical type, similar to that used in Part I[4], to correlate belt flexing life with tensile, aging and internal friction can be used with advantage:

$$\text{Life} = a + b(T - T_0) - cf$$

where $T - T_0$ is a reinforcement factor, which can be positive or negative, and T_0 is taken as 190 kg. per sq. cm. as a mean figure, f is the heat developed, a, b and c are constants.

Figure 2 (see also Table III) was constructed by using S^0 Shore hardness as a measure of heat development and plotting $(T - T_0) - 2S$ against fatigue life in

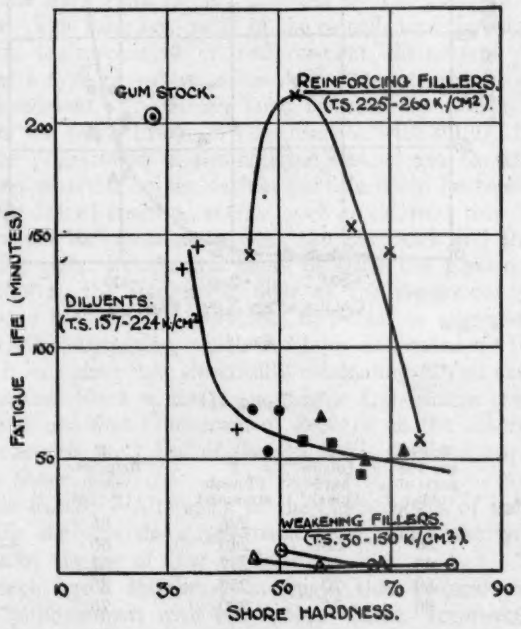

FIG. 1.

minutes. Most of the points are now brought on to a power curve of approximately parabolic shape. This indicates the general correctness of the empirical relation.

If other flexing lists were examined from this angle, it should be possible to predict an approximate value for the flexing life from the more elementary measurements of tensile strength, heat development and aging characteristics.

Parts I[4] and II[3] have been concerned with the direct evaluation of flexing life. The experimental data in this paper is directed mainly to an examination of reinforcement in relation to fatigue.

The two qualities fatigue and reinforcement are so often found in opposition in the practical design of rubber compounds for tires, that an understanding of their interaction is essential for the rapid development of compounds to meet all conditions. It is, therefore, necessary to consider the phenomenon of reinforcement in detail.

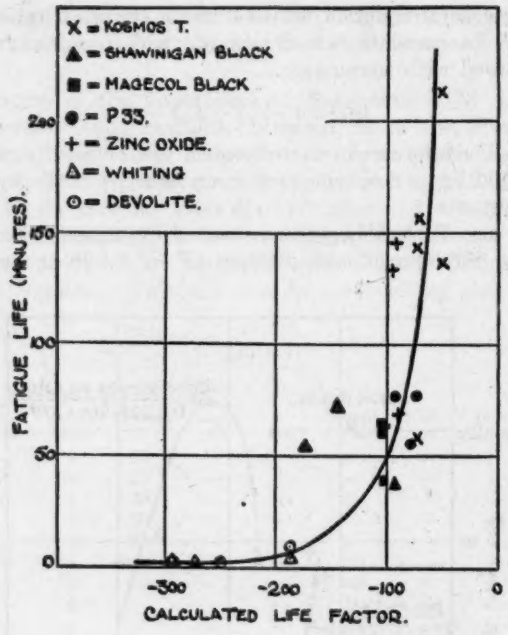

FIG. 2.

TABLE III

Main component	Parts per 100 parts of rubber	*S* (Shore hardness)	*T* (Tensile strength)	*K* Reinforcement (*T*-190)	*K*-2*S*	Minutes of fatigue life on Vogt machine
Gas black (Kosmos T)	20	45	225	35	— 55	139
	30	53	240	50	— 56	214
	40	63	247	57	— 69	153
	50	70	256	66	— 74	144
	60	75	260	70	— 80	56
Shawinigan black	30	58	157	— 33	— 149	71
	40	66	224	34	— 98	49
	50	72	163	— 27	— 171	53
Lamp black (Magecol)	30	54	197	7	— 101	60
	40	59	174	— 16	— 134	58
	50	65	164	— 26	— 156	41
P-33	30	45	200	10	— 80	74
	40	48	202	12	— 84	54
	50	50	194	4	— 96	74
Whiting	100	45	94	— 96	— 186	7
	200	58	41	— 149	— 275	1
	300	69	30	— 160	— 298	1
Devolite	100	50	105	— 85	— 185	10
	200	68	75	— 115	— 251	1
	300	81	73	— 137	— 299	1
Zinc oxide	50	34	159	— 31	— 99	134
	100	37	171	— 19	— 93	145
	150	42	182	— 8	— 92	65

Reinforcement.—The generally accepted definition of a reinforcing filler is one that improves the tensile strength and modulus of both unvulcanized and vulcanized rubber. Tested under suitable conditions it will be found that practically all fillers, even chalk, fulfil this condition. A narrower definition is that given by Blake[5], who pointed out that reinforcing fillers are those which do not reduce the tensile strength of the rubber when calculated on the actual cross-section at break. Under the second definition only a limited range of fillers fulfil the condition. The definition evolved in this paper narrows the number of fillers, which can be described as reinforcing fillers, down to a few. A true reinforcing filler may be described as a filler which tends to move the rubber from the rubbery state to the solid state even at low concentrations. This movement towards the solid state is best detected by the effect of high frequency on the resilience. This rules out many of the so-called reinforcing fillers.

With regard to the mechanism of reinforcement, the authors prefer to regard reinforcement as a type of vulcanization rather than to regard vulcanization as a type of reinforcement. The strong bond between the rubber and reinforcing particle acts like the sulfur bridge in vulcanization with sulfur. It was this view which led to the preparation of the chlorine treated gas blacks[6]. If the usual layer of adsorbed material on the carbon particle could be replaced by a layer of a material with latent chemical energy, such as chlorine, then it would appear that the bond could be increased between the gas black and the rubber. This proved to be the case. Reinforcing fillers decrease the resilience of rubber, a fact which points to the reinforcing filler as the continuous phase which is acting as the bond between the individual molecules or aggregates. Boiry[7] was the first to make this suggestion, which was later elaborated by Wiegand[8]. From this suggestion it was clear that electrically conducting rubber should be possible by selecting a carbon black of the correct shape and surface condition.

There is little doubt that reinforcement depends on the nature of the rubber (polarity, chain length, etc.) and of the gas black (surface, particle size distribution, particle shape, etc.).

Modifying the Rubber.—Alteration of the chain length of natural rubber by prolonged milling shortens the stress-strain curve. This shortening is to some extent overcome by the use of finer blacks.

Neoprene, which has a shorter chain length than natural rubber, does not give the same reinforcement with the rubber blacks. Improved reinforcement can be obtained by the use of fine blacks.

The fact that latex cannot be reinforced by gas black is probably connected with the larger particle size of the latex.

Modifying the Gas Black.—This may be effected by modifying ordinary gas black *in situ* by processing technique. The many systems of preparing black compounds, such as repeated cooling and milling, the Firestone method of heating black master batches, the use of mixed blacks of varying particle size and so on are all examples of this procedure.

It may also be brought about by modifying the black during production or after production but before use in the rubber industry. Included in this class is the everyday technique of the rubber black manufacturer who adjusts his conditions of production to give the best reinforcing black. In addition, various attempts have been made to modify the black after production by heating and cooling in various gases. For the reason given earlier in this paper after-treatment with chlorine was studied. It was found that this tightly bound chlorine brought about desirable changes in the properties of the black. It

retards the acceleration of cure usually found in heat-treated blacks but gives a higher tensile strength, and higher resilience without any reduction in resistance to abrasion as measured on a laboratory machine. Road tests are in progress. Table IV illustrates the effects on the physical properties of the rubber tread vulcanizate shown below:

Rubber	100 parts	Stearic acid	3 parts
Zinc oxide	5 "	Sulfur	3 "
Carbon black	40 "	Mercaptobenzothiazole	0.75 "

Vulcanization: 45 min. at 141° C. for untreated black
55 " " " " treated "

The above sample of chlorine-treated black contained 4.5 per cent chlorine and shows considerably lower heat development on flexing, as endorsed by longer running before burst occurs on the Martens-Schopper ball burster. Further experiments were done on another sample of black containing 12 per cent of chlorine, compounded into a rubber tread vulcanizate containing 47.5 parts of black per 100 of rubber). This compound was run on the Martens-Schopper machine and the temperature taken with a thermoneedle after 2,000 revolutions in the track. This temperature was found to be about 40° C. below that of the control sample.

TABLE IV

Vulcanizate	Relative abrasion loss per hour	Resilience at optimum cure %	Tensile strength at optimum cure kg. per sq. cm.	Martens Schopper test revolutions
From treated carbon black.....	0.105	70.1	305	10,300
From untreated carbon black....	0.105	62.8	278	1,150

THEORY

It has been shown by a number of workers, including particularly Gemant in the field of dielectrics, that the intermediate state between liquid and solid can be well represented by a complex viscosity. This idea has also been put

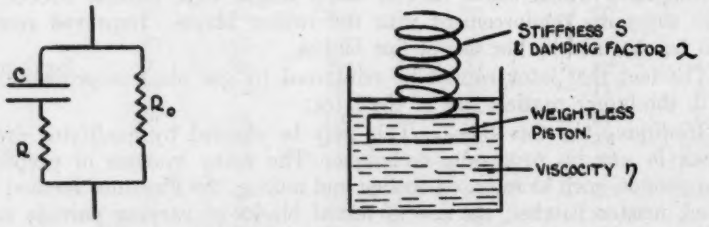

FIG. 3.

forward by Healey[9] as a mechanical model of rubber. These conceptions are represented diagrammatically in Fig. 3. The behavior of the mechanical model is most easily obtained by studying the electrical analog, as our knowledge and technique for solving electrical alternating current problems is much greater

than our corresponding knowledge of mechanical vibrations. The main features of such a circuit are that it has a variable impedance with frequency or in mechanical terms the viscosity changes with frequency, as do also modulus and resilience. A glance at the circuit will show that at very high frequencies the behavior is akin to that of solid body with some fixed internal friction. At low frequencies, such as occur in cold flow experiments on rubber, the circuit is effectively a plain resistance or in mechanical terms a true viscous fluid with no stiffness. Such a simple circuit, without going into detail, does not represent the behavior of rubber quantitatively, but it does predict the following observed effects noted in Part II[3], the increase of modulus with frequency; the fall in viscosity with rise in frequency, reaching a steady value at high frequencies;

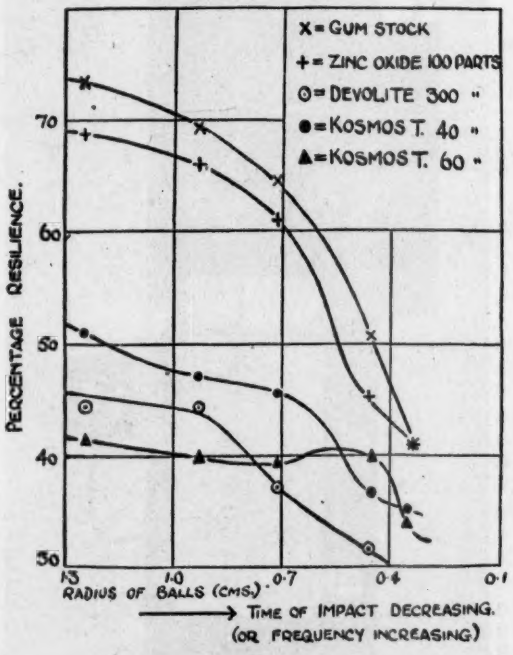

FIG. 4.

and the fall in resilience at high frequencies with a maximum at some intermediate frequency.

There exist three methods for studying the alteration of properties of rubber with time of impact: by impact tests, free oscillations and forced oscillations. The first method is the easiest to demonstrate and is one widely used for testing purposes, though the hardest to use quantitatively from a frequency standpoint, since the time of impact varies with the modulus of material and is not easy to measure, especially at very high speeds. Figure 4 is included for sake of completeness, and indicates the variation in resilience with size of ball dropped from a standard height. In every case resilience falls markedly with decreasing time of contact or decrease in ball size.

Free oscillations were tried as a testing method and are described in Part I[4]. Their main limitation is that those which are easy to measure are too slow and those which are fast enough are as difficult as impacts for experimental purposes.

Figure 5 represents a rather faster type of free-oscillation apparatus, corresponding in some respects with other pendulum instruments, with a stress cycle of about one-half second or less, according to the moment of inertia of the system.

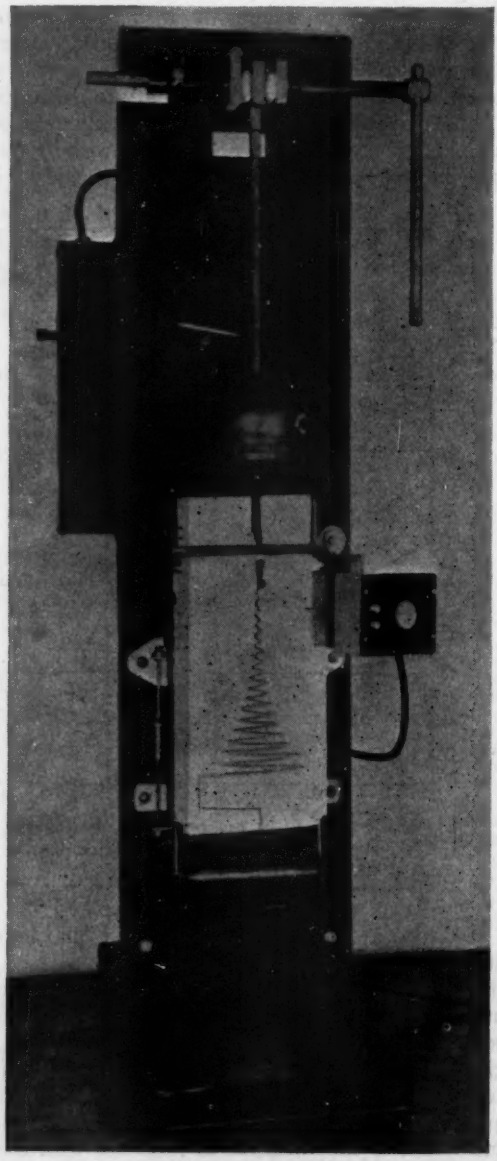

FIG. 5.

Forced oscillations have only one serious limitation: their relatively small amplitude, except at resonance. The work in this paper is based on a study of forced oscillations under conditions of resonance.

Experimental Method.—The theory and description of the apparatus has already been fully given in Part II[3]. It has been argued that the frequencies obtained with this apparatus are too high. This is to some extent true, but it should be kept in mind that quite a number of machines of practical everyday as well as of military importance work at frequencies within this range. Work is however now in progress to modify the apparatus for use at lower frequencies. Meantime, the apparatus has been found to be of the greatest use on the design of mountings for machines generating high frequency impulses.

In the present communication the apparatus has been used to study the effects of a number of common fillers upon the physical properties of rubber at high frequencies.

TABLE V

GAS BLACK: VARIATION OF MODULUS AND RESILIENCE WITH FREQUENCY

Kosmos *T* per 100 parts of rubber	Frequency cycles per sec.	Mass gm.	$F/X \times 10^8$ dynes per cm.	$S \times 10^9$ dynes per cm.	γ kg. per sq. cm.	Resilience %
0	80	1112	0.171	0.281	23.5	82.7
	135	408	0.215	0.294	24.5	79.4
	200	202	0.290	0.320	26.7	75.2
	290	97	0.405	0.322	26.9	67.4
20	120	1112	0.375	0.630	52.5	82.9
	205	408	0.51	0.675	56.2	79.2
	295	202	0.64	0.695	58.0	75.3
	445	97	0.77	0.758	63.1	73.1
	160	1112	0.80	1.120	93.3	80.0
30	275	408	0.92	1.220	101.8	79.2
	400	202	1.15	1.280	106.4	75.4
	600	97	1.50	1.380	115.0	71.0
	210	1112	1.26	1.930	161.0	81.4
40	355	408	1.56	2.025	169.0	78.4
	520	202	1.72	2.150	179.0	77.9
	770	97	2.06	2.250	187.0	74.8
	250	1112	1.47	2.730	228.0	85.0
50	430	408	1.93	2.960	247.0	82.3
	620	202	2.13	3.050	254.0	80.2
	975	97	2.35	3.450	288.0	80.6
	295	1112	1.61	3.820	318.0	87.6
60	500	408	2.17	4.030	336.0	84.5
	750	202	2.87	4.500	375.0	81.9
	1170	97	3.10	5.200	434.0	82.9

Experimental Results.—Tables 5 and 6 and Figures 6 to 10 show the results obtained with the following fillers (the detailed mixings are given in Table 2) 0-60 parts of gas black; 30-50 parts of lamp black; 50-150 parts of zinc oxide; and 100-200 parts of china clay. An examination of the results is best undertaken by considering first the variation of dynamic modulus and then the variation of dynamic resilience with frequency. A further subdivision of results is made into gas black and other fillers.

DYNAMIC MODULUS

(*a*) *Gas Black* (*Figure* 6).—With the addition of gas black to rubber the dynamic modulus increases rapidly until with 60 parts by weight, the modulus is more than ten times that of the unloaded compound.

The modulus-frequency characteristic gets steeper with increasing gas black content.

The percentage change in modulus (see Figure 10) over the frequency range decreases to a minimum with 40 parts of gas black on 100 parts of rubber and thereafter increases.

TABLE VI

OTHER FILLERS: VARIATION OF MODULUS AND RESILIENCE WITH FREQUENCY

Filler	Parts per 100 parts rubber	Frequency cycles per sec.	Mass gm.	$F/X \times 10^8$ dynes per cm.	$S \times 10^9$ dynes per cm.	γ kg. per sq. cm.	Resilience %
		90	1112	0.202	0.357	29.7	83.7
	50	148	408	0.276	0.355	29.5	78.3
		217	202	0.366	0.380	31.7	74.0
		312	97	0.487	0.384	32.0	66.5
		100	1112	0.265	0.440	36.7	82.8
Zinc oxide	100	170	408	0.386	0.473	39.5	77.5
		240	202	0.490	0.475	39.7	72.3
		350	97	0.571	0.500	41.6	69.8
		112	1112	0.357	0.555	46.3	81.5
	150	187	408	0.482	0.575	48.0	76.8
		262	202	0.62	0.573	47.8	71.2
		385	97	0.81	0.631	52.7	67.0
		125	1112	0.394	0.680	56.8	83.3
	30	212	408	0.522	0.722	60.2	79.7
		310	202	0.654	0.762	63.6	76.0
		460	97	0.775	0.810	67.6	74.0
		145	1112	0.517	0.920	76.8	83.8
Magecol lamp black	40	245	408	0.742	0.961	80.1	78.3
		350	202	0.888	0.980	81.5	75.1
		530	97	1.10	1.066	89.0	72.0
		168	1112	0.81	1.236	94.7	81.4
	50	280	408	0.958	1.264	97.1	78.3
		410	202	1.12	1.350	112.3	77.0
		615	97	1.64	1.438	119.7	70.1
		130	1112	0.614	0.742	62.0	77.1
	100	220	408	0.697	0.780	65.0	75.6
		320	202	0.89	0.835	69.5	71.6
		485	97	1.23	0.930	77.5	66.0
Devolite		225	1112	1.88	2.180	182.0	76.3
	200	370	408	1.80	2.140	178.0	76.7
		570	202	2.77	2.530	211.0	70.1
		860	97	3.43	2.840	237.0	68.4

(*b*) *Other Fillers* (*Figure* 7).—*Zinc Oxide.*—The addition of zinc oxide makes little difference to the modulus, even at 150 parts on 100 of rubber.

Lamp Black.—Lamp black in quantities up to 50 parts has a certain stiffening effect, but markedly inferior to equal volume loadings of gas black, and the curves are less steep with change in frequency.

Devolite China Clay.—Two hundred parts of Devolite gives a very similar curve to that for 40 parts of gas black. One hundred parts, however, gives a relatively soft compound.

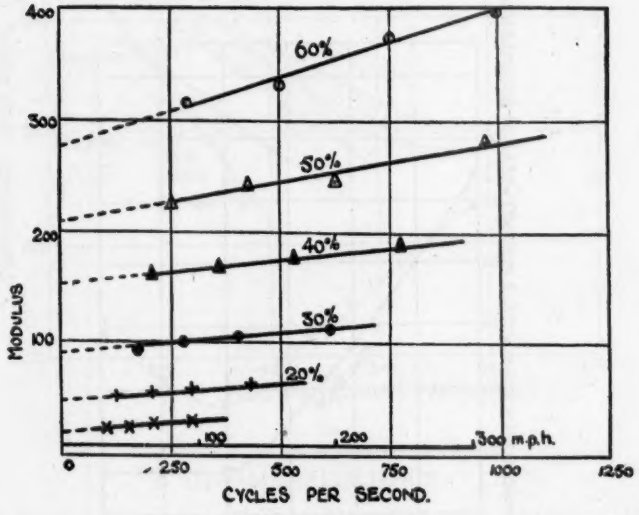
60%
50%
40%
30%
20%
MODULUS
100
200
300
400
100
200
300 m.p.h.
0
250
500
750
1000
1250
CYCLES PER SECOND.

FIG. 6.

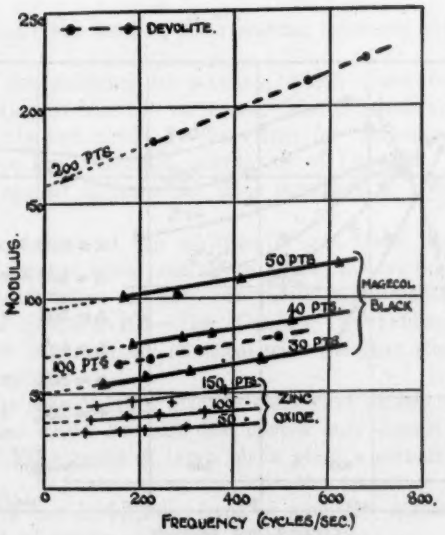
DEVOLITE.
200 PTS.
50 PTS.
40 PTS.
30 PTS.
100 PTS.
150 PTS.
100
80
MAGECOL. BLACK
ZINC OXIDE.
MODULUS.
0
200
400
600
800
FREQUENCY (CYCLES/SEC.)

FIG. 7.

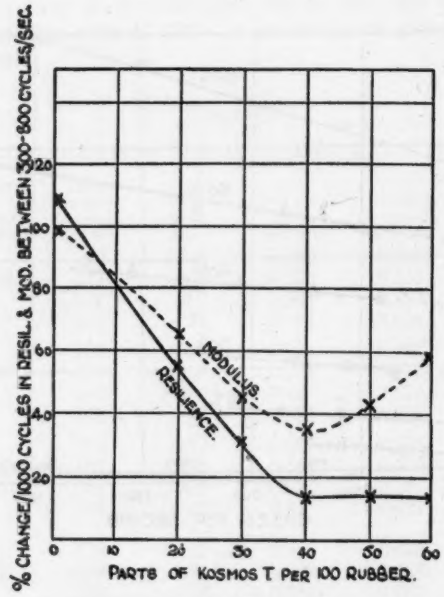
% CHANGE/1000 CYCLES IN RESIL. & MOD. BETWEEN 300-800 CYCLES/SEC.
120
100
80
60
40
20
0
10
20
30
40
50
60
MODULUS
RESILIENCE
PARTS OF KOSMOS T PER 100 RUBBER.

FIG. 8.

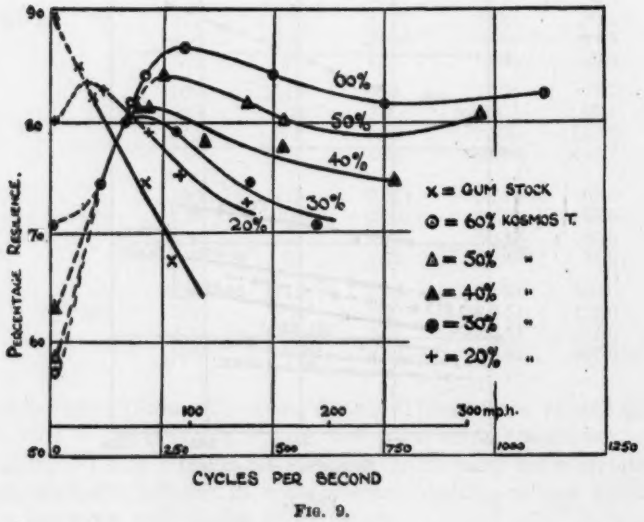
PERCENTAGE RESILIENCE.
90
80
70
60
50
60%
50%
40%
30%
20%
X = GUM STOCK
⊙ = 60% KOSMOS T.
Δ = 50% "
▲ = 40% "
● = 30% "
+ = 20% "
100
200
300 m.p.h.
0
250
500
750
1000
1250
CYCLES PER SECOND

FIG. 9.

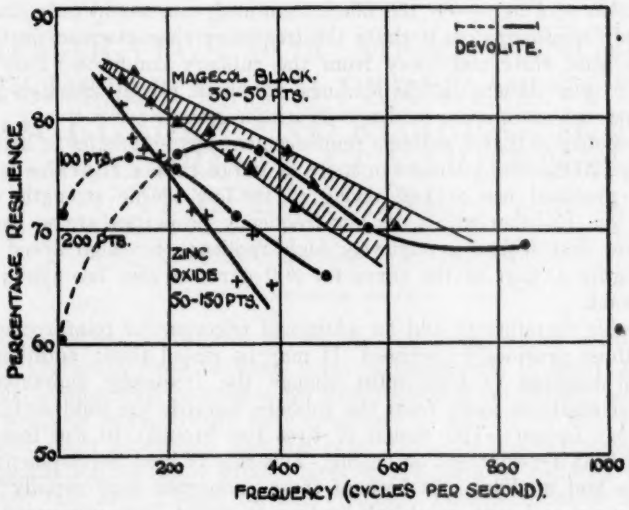

FIG. 10.

DYNAMIC RESILIENCE

(*a*) *Gas Black* (*Figure* 9).—Resilience decreases with frequency above 300 cycles per second in all cases, the curves getting less steep with increasing parts of black.

With increasing gas black loading the resilience increases above 150 cycles per second.

All curves show the existence of maxima, which move towards higher frequencies as the loading of black is increased. The maxima are indicated partly by experimental points and partly by the values for resilience at zero frequency (or near) found with the pendulum instrument of Figure 5.

All compositions appear to have the same resilience at 150 cycles per second or near.

Below 150 cyles per second the addition of gas black lowers the resilience of rubber, so far it has not been possible to cover this region satisfactorily with the apparatus; the difficulties are however purely experimental and can be met.

(*b*) *Other Fillers* (*Figure* 10)—*Zinc Oxide.*—The resilience of compounds containing zinc oxide is practically identical with the gum stock values over the whole frequency range.

Lamp Black.—The case of lamp black is somewhat intermediate between that of gas black and zinc oxide, but still the curves only depart slightly from unloaded compounds. Fifty parts of lamp black gives a similar curve to that for 30 of gas black.

China Clay.—Here one finds indications of resilience maxima, as in the case of gas black, though of course only with high loadings.

CONCLUSIONS

The modulus-frequency and resilience-frequency characteristics give valuable information for the classification of fillers and the mode of action and for engineering design of rubber articles subjected to high speed stressing.

Classification of Fillers.—Of the fillers examined, one would only classify gas black as truly reinforcing, as it shifts the frequency characteristics in the direction of the solid state and away from the rubbery condition. Zinc oxide is practically a pure diluent in the loadings examined. Lamp black is an intermediate type and gives some evidence of reinforcement.

Clay is peculiar in that it exhibits reinforcement characteristics in high volume loadings, *e.g.*, 200 parts by weight or more in 100 of rubber. But this fact makes it of little practical use as yet, owing to its low tensile strength and high permanent set. In other words, its low frequency properties are so bad that it matters little that it has a relatively high resilience for high speed impacts. Thus, in Figure 4, part of the curve for 300 parts of clay lies above that for 60 of gas black.

It is possible therefore to add an additional criterion for reinforcement to be used with those previously discussed. It may be stated thus: addition of relatively small loadings of filler must change the frequency characteristics of modulus and resilience away from the rubbery towards the solid state.

Engineering Design.—The design of tires has brought to the fore the importance of heat development on flexing. This rate of heat development depends on resilience and modulus. As both of these properties vary rapidly with frequency or speed and with gas black loading, it would seem important to make the measurements at frequencies corresponding to speeds in actual service.

On Figures 6 and 9 a scale of m.p.h. is included, based on a simple calculation. Its accuracy may be about a factor of two, according to the assumptions made, as to tire contact area with the road and its variation with speed.

Figure 8 indicates that 40 parts of gas black show the least alteration of properties with frequency at high speeds. This may be the reason for the technical optimum somewhere in this region. A balance has been effected between the rubbery and solid states which is not very sensitive to the type of stress applied. This is only true for dynamic conditions and probably above 30 m.p.h.

This may also explain the inferior running of tire tread compounds at very low speeds, *e.g.*, in footwear.

In conclusion, one may summarize the significance of the work described in this paper by saying that it emphasizes the importance of the time and frequency factors in rubber testing. Most rubber testing machines, such as the Schopper tensile tester, and most flexing tests are performed in a time which bears little relation to ordinary service conditions. Honorable exceptions are the Goodrich flexometer and the Dunlop pendulum, which correspond to stress frequencies of the order 30 and 25 cycles per second, respectively. In the future it is desirable that more attention be paid to developing tests which are performed in a time and at a frequency corresponding to service conditions.

In conclusion, the authors wish to express their thanks to Imperial Chemical Industries, Limited, in whose Rubber Service Laboratories the work was conducted, for permission to publish the results embodied in this paper.

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[9] Healey, *India-Rubber J.* **69**, 57 (1925).

AN APPARATUS FOR MEASURING COMPRESSIBILITY AND PERMANENT SET OF RUBBER AND RUBBER-LIKE MATERIALS AT VARIOUS TEMPERATURES *

H. A. HOEKSTRA and J. HOEKSTRA

VENLO, AMSTERDAM, HOLLAND

Introduction.—The importance of rubber and rubber-like substances for packings as shock-absorbers between parts of machinery, in short, the use of rubber under compression in mechanical construction is continually increasing.

Several methods have already been proposed to investigate the behavior of rubber under these conditions, and the most ingenious method seems to be a two-dimensional stretching of rubber films in the form of balloons (Sheppard and Clapson, *Ind. Eng. Chem.*, **24**, 782 (1932)). This deformation is identical to homogeneous compression if volume changes by the deformation may be disregarded. The latter does not hold true if inactive fillers are used, which give rise to vacuoles in stretching but not in compression.

However, in practice homogeneous compression is rare, as the material will never be able to glide without friction along the compressing parts to which in many cases the rubber is vulcanized. Because of the complicated deformation of rubber in practice, it is necessary to imitate the real conditions under which compression takes place.

For these reasons a simple compression of cylindrical specimens between parallel plates was chosen as a first basis for the investigations.

In determining compressibility of rubber in this way, the only difficulty which has to be overcome results from the gliding of the specimen along the surface of the compressing dies. For the rest, the construction of a compression-dynamometer that could be placed within an ordinary thermostatic oven can be realized without difficulty. The measurement of permanent set does not give rise to problems other than the gliding just mentioned. One of two ways for the determination of permanent set may be chosen: compressing to a certain deformation or compressing under a fixed load. Both ways are in themselves equally satisfactory, the results bearing relations to the different uses of the rubber. If a measurement is standardized which lies between the two principles (fixed compression and fixed load) by prescribing the compression to a definite extent of a steel spring, objections might be raised. In this case the compressing force will lessen, as the specimen is slowly decreasing in thickness in the course of the test. In this way, by using a spring or similar device, a new arbitrarily fixed, though definite, factor is introduced into the determination of permanent set. However, this arbitrarily fixed factor can be, and therefore should be, eliminated.

The need of an adequate apparatus is obvious if an insight is desired into the mechanism of relaxation in compressed bodies of rubber and of rubber-like materials. In this case it becomes necessary to measure the trend of pressure

* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 14, No. 6, pages 382-388, April 1939.

while the specimen is compressed to a certain constant extent and to measure the progress of flow when the specimen is under constant pressure. Although the last-mentioned determination can be carried out by means of one of the several compression-plastometers now in common use in the rubber and plastics industries, these instruments are in general not suited for the high compressing forces which seem desirable in dealing with vulcanized stock of high quality.

It was with the purpose of making an investigation into the hysteresis and permanent set of compressed rubber at different temperatures that A. van Rossem and D. J. van Wijk, of the Netherlands Government Rubber Institute at Delft, Holland, asked for the writers' advice in the construction of an apparatus fulfilling these requirements.

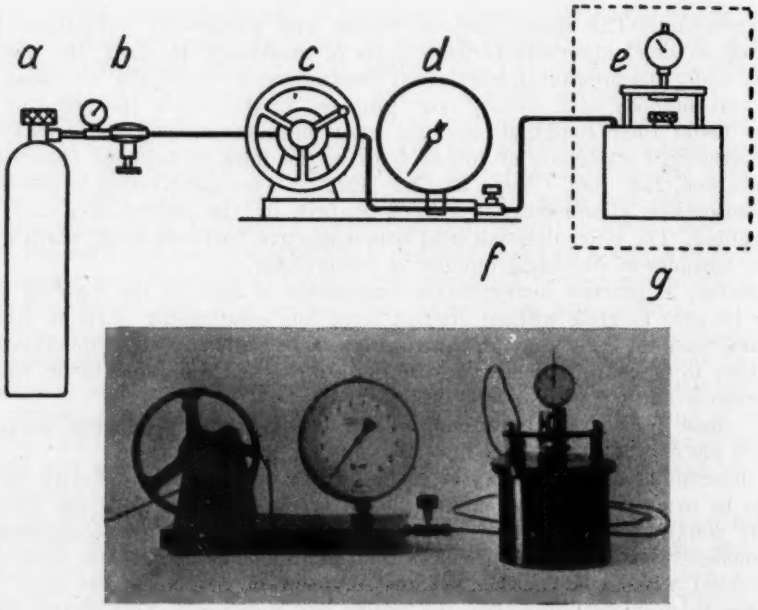

FIG. 1.

The instrument which has resulted from this collaboration will now be described and, in addition, some determinations obtained at the Netherlands Government Rubber Institute by means of the instrument will be given.

Principle of Instrument.—The apparatus consists in principle of two parallel plates, of which the upper one can be moved downwards with any force up to 500 kg. This movement is caused by a special pneumatic device. The case of the instrument bears a gauge for measuring at any time the displacement of the upper plate. The special device for the movement of the lower plate consists of a corrugated metal box of very low hysteresis. By using this frictionless metal box instead of a cylinder and piston the compressing force is directly derived from the pressure within the box. A sensitive pressure-regulator keeps the pressure constant or varies it as required during the experiment.

Description of Instrument.—The whole apparatus (Figure 1) consists of a pneumatic ram (*e*), a pressure regulator (*c*) with precision pressure gauge (*d*)

and a compressed air cylinder (*a*) with reducing valve (*b*). Of these components the pneumatic ram only needs to be put in a thermostatic oven (*g*) if determinations at definite temperatures are to be made.

Pneumatic Ram.—The instrument is constructed in such a way that the stresses in the instrument, induced by the rather high compressing forces, do not affect the indication of the thickness gauge. This result is obtained by fixing the metal box (*a*) (see Figure 2) underneath the lower plate (*b*). The lower end of the box (*a*) is soldered to a plate (*c*), which carries a frame consisting of two bars (*d*) connected by rods (*e*). The upper bar carries the upper plate (*f*). By this construction the forces on both sides of the lower plate (*b*) are fully counterbalanced.

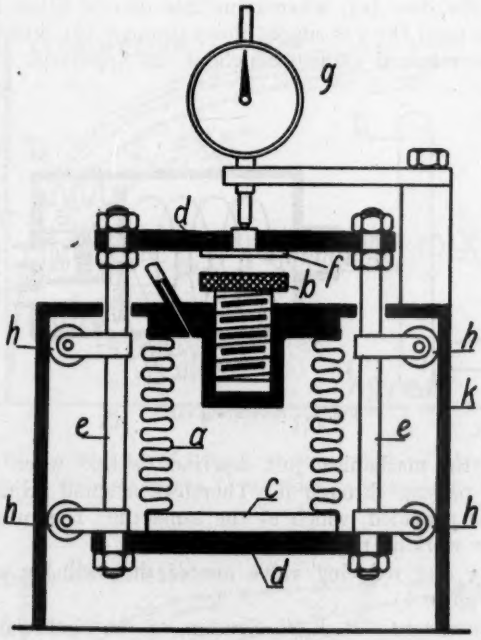

FIG. 2.—Pneumatic ram.

The free movement of the upper plate (*f*) is 5 mm. and the maximum clearance between the plates can be varied by the adjustable lower pltae (*b*) from 0-16 mm. The thickness gauge (*g*) is centrally located over the upper plate (*f*). The dial of this gauge is divided into hundreds of a millimeter and has a range of 5 mm. The movement of the box (*a*) and of the frame (*d*, *e*) is controlled by means of two sets of ball-bearing rollers (*h*), rolling along the inside of case (*k*).

To reduce the volume of compressed gas needed to inflate the box (*a*), it is almost completely filled with a suitable liquid.

Pressure Regulator.—The regulator enables the operator to adjust, increase or decrease the pressure on the specimen under investigation, at any time, at any rate and with great precision. The mechanism of the regulator (U. S. patent 2,092,844) is shown in Figure 3. The gas supply is connected at (*g*) to the

regulator and the pneumatic ram through the pressure gauge (see Figure 1) is connected at (*k*). The spring is compressed by means of the handwheel (*a*). This spring acts on a corrugated metal box (*d*) and is counterbalanced by the gas pressure within this box. The inside of the box is directly connected with the pneumatic ram and the working pressure is read on the pressure gauge (see (*d*) in Figure 1).

If the compression of spring (*c*) is decreased or if the gas pressure in box (*d*) increases (*e.g.*, by thermal expansion of the ram), tube (*h*) moves to the left, the valve (*e*) shuts off the gas inlet (*g*) from the gas supply, the gas from box (*d*) escapes through the interspace between valve seating (*i*) and tube (*h*) and reduces the pressure through (*k*) on the pneumatic ram. If, on the contrary, the gas pressure decreases, the box (*d*) contracts towards the right and tube (*h*) is closed by the disc (*e*), whereupon this disc is lifted from the valve seating (*i*) and gas from the gas supply flows through (*g*) into the box to raise the pressure to the required value throughout the apparatus.

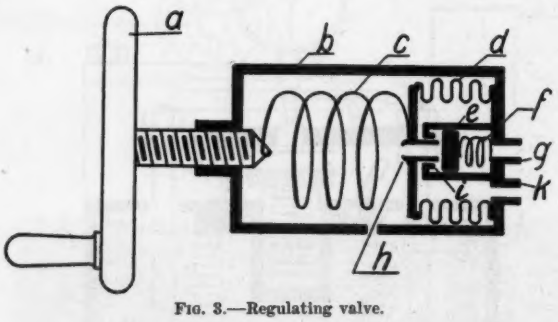

FIG. 3.—Regulating valve.

The working of the mechanism just described is best when a slight flow of gas is continually passing through it. Therefore a small adjustable leak (see (*f*) in Figure 1) is provided, which at the same time is required in adjusting the pressure at low working pressures in the ram.

The gas cylinder and reducing valve are of the ordinary commercial type (see (*a*), (*b*) in Figure 1).

Tests on the Instrument.—P. J. W. Soudijn, of the Netherlands Government Rubber Institute, carried out a number of tests to determine the accuracy of the instrument and its inherent hysteresis. The writers are kindly permitted to reproduce some of his results.

The readings of the pressure gauge were checked against those of a subsidiary pressure gauge attached to a small metal box, completely filled with a fluid, which is fitted between the plates of the pneumatic ram. The readings (in kg. per sq. cm.) of the pressure gauge, multiplied by the equivalent of the surface of the metal bellow in the pneumatic ram (50 cm.) and corrected for the relatively small force, needed to deform the metal bellow in the pneumatic ram, were found to agree with the force between the two plates. Deviations were found to be of the same order as the accuracy of the readings, namely, within 2 to 3 kg., of a force of 500 kg. This order of accuracy remained true when the pressure in the ram was not kept constant, but was steadily increased or decreased at a rate of 1 kg. per cm. per minute, that is, the apparatus showed no appreciable hysteresis (see Figure 4).

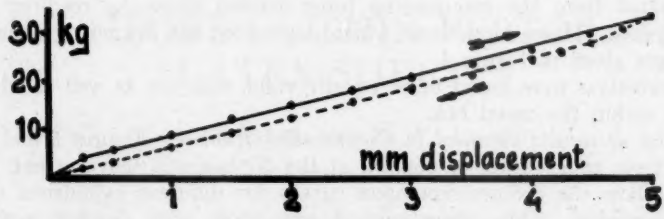

FIG. 4.—Corrections due to displacement of lower plate (force needed to deform the metal box in the pneumatic ram).

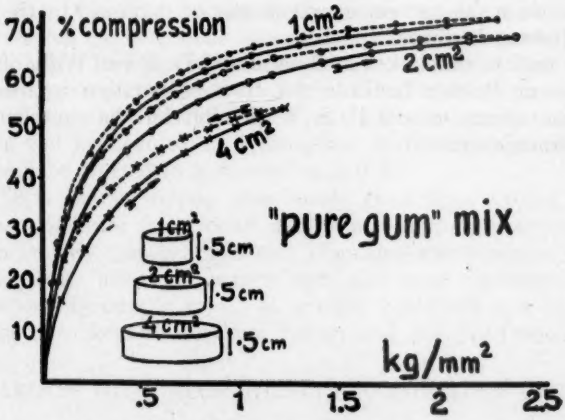

FIG. 5.—Hysteresis of different samples of vulcanized rubber.

(Rubber, 100; sulfur, 3; diphenylguanidine, 1; zinc oxide, 3; vulcanized for 30 min. at 147° C.).

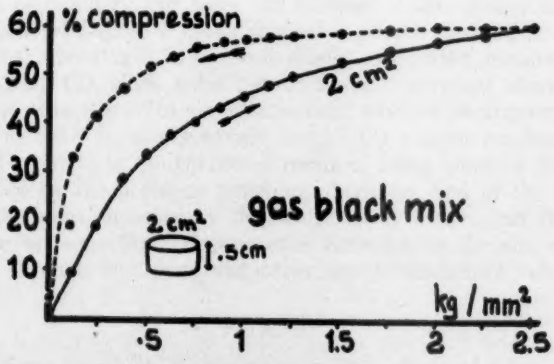

FIG. 6.—Hysteresis of vulcanized mix.

(Rubber, 100; sulfur, 3½; diphenylguanidine, 1½; Micronex, 30; zinc oxide, 10; mineral rubber, 8; stearic acid, 2; spindle oil, 2; vulcanized for 45 min. at 147° C.).

As stated above, the force needed to deform the metal box in the ram must be subtracted from the compressing force derived from the readings of the pressure gauge. These corrections, which depend on the degree of extension of the box, are given in Figure 4.

The corrections were found to be equally valid with low as well as with high pressures within the metal box.

Examples of results obtained in Compressing Rubber.—Figures 5 and 6, also resulting from experiments of Soudijn at the Netherlands Government Rubber Institute, show the compression-stress curves for different cylindrical discs of vulcanized rubber. These discs were 5 mm. high, with circular surfaces of 1, 2 and 4 sq. cm.

Great differences in hysteresis of the rubber on compressing and releasing are shown between the pure gum and gas black mixes. Further experiments made with the use of the instrument will shortly be published by the Netherlands Government Rubber Institute.

The writers wish to thank A. van Rossem and D. J. van Wijk, of the Netherlands Government Rubber Institute, for their coöperation regarding the construction of the apparatus and P. J. W. Soudijn for the experiments referred to in this communication.

MULTIPORE—A THIN PERFORATE LATEX SHEET *

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Charles Goodyear, who perhaps anticipated more fully the versatility of rubber than anyone since his time, suggested in his treatise on rubber[1] that perforated rubber might be used for "sieves, colanders and strainers" and that it might "also be substituted in a great many cases, if not generally, for woven wire cloth." With the need for products of this type intensifying in recent years, much research has been done toward improving the processes and products related to this field. Two recently developed porous sheet rubber products are Multipore[2] and microporous hard rubber[2]. Both have extensive application as aids to filtration, and each has other potential uses peculiar to itself. The present article will be devoted to a discussion of Multipore, and microporous hard rubber will be treated in a succeeding article.

Multipore[3] is a porous rubber sheet made from latex rubber, and derives its porous characteristics from many minute and uniformly spaced holes that extend perpendicularly through the sheet. The types now produced commercially have 1,100 to 6,400 holes per square inch and poor diameters of 0.012 to 0.004-inch, depending on the type. At present Multipore can be obtained in soft rubber, hard rubber, flexible hard rubber and soft Neoprene.

COMPARISON WITH MECHANICALLY PERFORATED SHEETING

While to the casual observer Multipore resembles a perforated sheet with an unusually large number of exceedingly fine holes, Multipore is not and should not be considered in the same class with mechanically perforated sheeting. The holes in Multipore are not punched, but are formed by the expansion of air through a film of liquid rubber latex. As a result of the unique features of the process[4] by which Multipore is manufactured, a porous sheeting is now available which has many advantages over mechanically perforated material, including: (1) smaller holes; (2) more holes per unit area (punched sheeting is rarely made with more than 500 holes per square inch; whereas Multipore can be made with as many as 6,400 holes per square inch); (3) greater mechanical strength (this increased strength is the combined result of using latex, of the elimination of cuts produced by the ordinary punching operation, and of the natural reënforcement of the holes imparted by the Multipore process); and (4) production of holes before vulcanization (this permits variation in the shape and porous characteristics through stretching and other operations before vulcanization).

PROCESS

The master form on which Multipore is made consists of a heavy fabric belt surfaced on one side with a layer of rubber and known as a Multipore blanket. The rubber surface appears to be full of small round holes uniformly spaced. Actually these holes are pits approximately 0.020-inch deep and closed at the

* Reprinted from the *India Rubber World*, Vol. 100, No. 5, pages 33-36, August 1, 1939.

bottom. The number of pits per unit area and the diameter of the pits at the surface of the blanket determine the porous characteristics of the Multipore made on it and are subject to control in regard to both size and number per unit area.

For commercial production of Multipore the master blanket is placed, with the pitted surface up, as an endless belt on a modified conventional spreading machine. An elevation sketch of the equipment used in the process is shown in Figure 1. A thin layer of liquid rubber latex is applied to the moving belt by a spreader bar. The latex completely covers all the pits in the blanket surface, but does not run down into them. Thus air is trapped in each little pit. Heat is then applied to the under surface of the blanket by a steam platen, and as the belt becomes hot, the air in the pits expands, blowing little bubbles in the film of latex. When the bubbles burst, small holes are left in the film of rubber corresponding in size and number to the pits in the blanket surface. This is illustrated in Figure 2 by microphotographs of the blowing process taken with

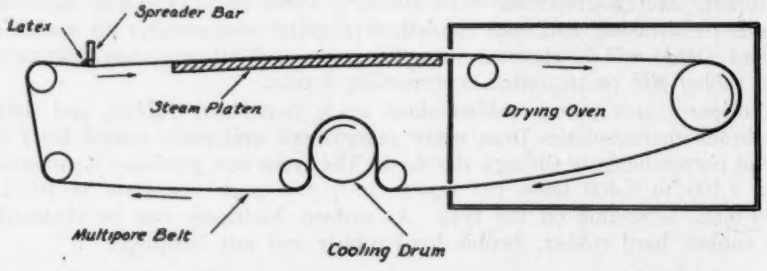


FIG. 1.—Sketch of spreader showing essential features of process for manufacturing multipore.

a moving picture camera, which show the development of the bubbles by air expanding in the pits beneath.

The blown rubber film is then thoroughly dried in the drying chamber; the belt is cooled to room temperature on a cooling drum, and the process is repeated as many times as are required to obtain the desired thickness. In this manner a sheet of Multipore can be made to any thickness between 0.005- and 0.100-inch, to a tolerance of a few thousandths of an inch.

The sheet of Multipore, having holes that extend all the way through, is then stripped off the master blanket and vulcanized. Between 95 and 100% of the holes in the Multipore blanket are reproduced in the Multipore sheet. As would be expected from a consideration of the process, the perforations in Multipore are not truly cylindrical in shape, but are reënforced internally by slight constrictions which contribute to strength and tear resistance. The shapes of the pores obtained by the Multipore process and by mechanical perforation, respectively, are illustrated by the microphotographs in Figure 3.

TYPES OF MULTIPORE

There are two general types of Multipore, plain and expanded. As indicated below, each type gives promise of adaptability for a wide variety of products.

PLAIN MULTIPORE

If after stripping, the Multipore sheet is vulcanized without any further processing, the product is classified as plain Multipore. In this form the holes

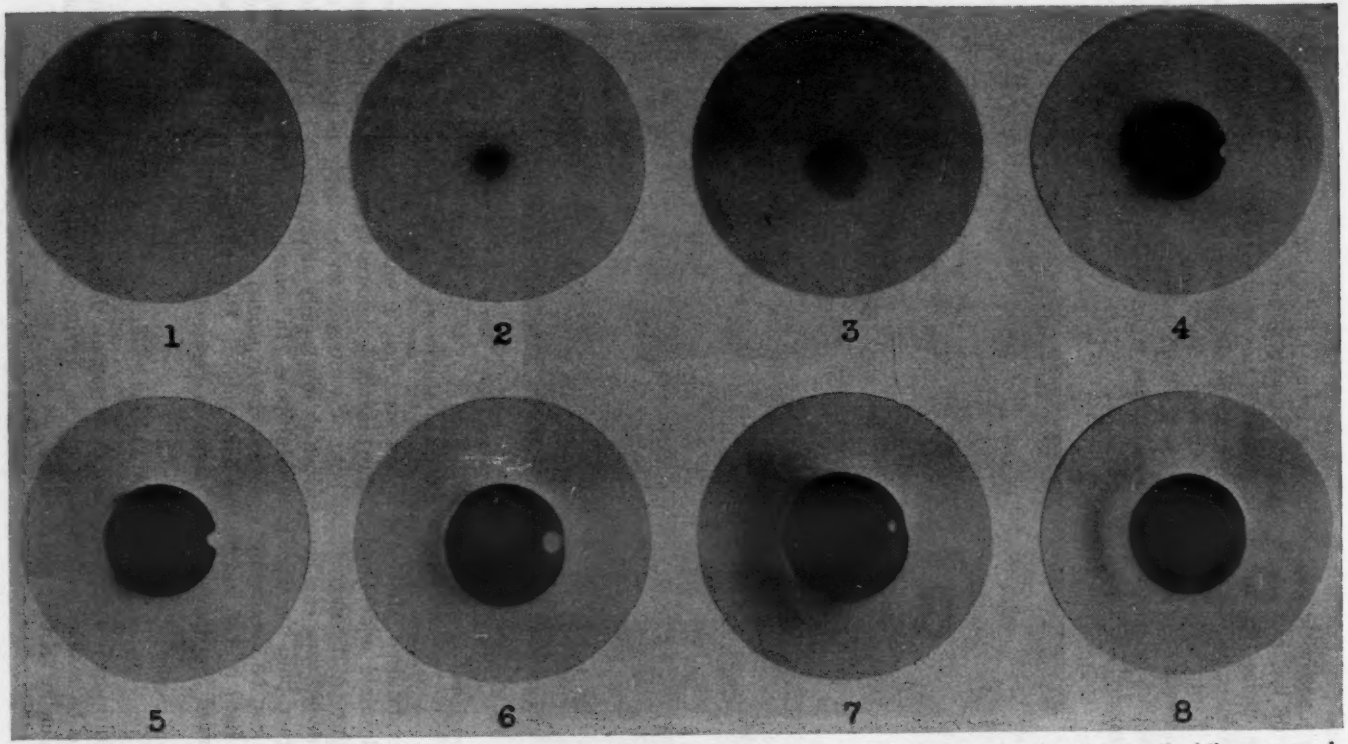


FIG. 2.—Microphotographs (48 magnifications) of stages in blowing of Multipore: 1, wet latex film immediately after spreading; 2-6, growth of the pore caused by the entrapped air expanding as it is heated; 7, film drying out with the bubble about to break; 8, bubble has broken and the latex is "set".

are round and extend perpendicularly through the sheet. Plain Multipore can also be made with a fabric backing firmly adhered to one or both sides with very little loss in porosity. A wide variety of fabrics can be used, and by a suitable choice the stretchable characteristics of the rubber-fabric combination may be controlled. Plain Multipore can be obtained in soft rubber, hard rubber, flexible hard rubber and soft Neoprene. Microphotographs of two types of plain Multipore are shown in Figure 4. Table I summarizes the porous characteristics and maximum dimensions of the standard types of plain Multipore now commercially available.

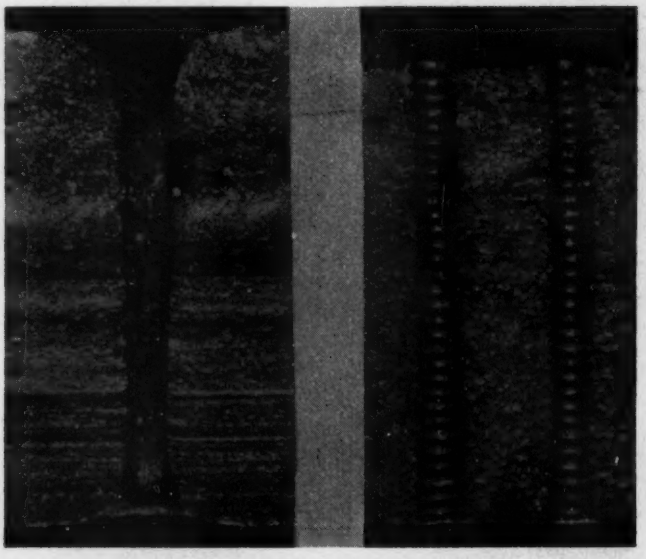


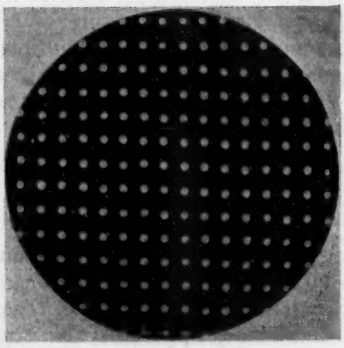
FIG. 3.—Cross-sectional view of holes (magnified 31 diameters): (*left*) punched sheet; (*right*) Multipore.

EXPANDED MULTIPORE

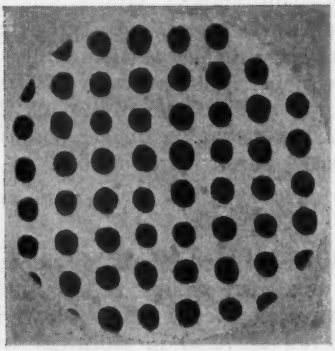
If unvulcanized Multipore is first stretched in either one or two directions and vulcanized under stretch, the product is known as expanded Multipore[5]. Depending on the degree and type of stretch, a wide variety of products of the expanded type can be made which are usually characterized by oval holes and higher porosity than plain Multipore. In some cases porosities as high as 30% can be obtained. At present the expanded types can be made in soft rubber, hard rubber and flexible hard rubber. Microphotographs of two types of expanded Multipore are also shown in Figure 4.

APPLICATIONS

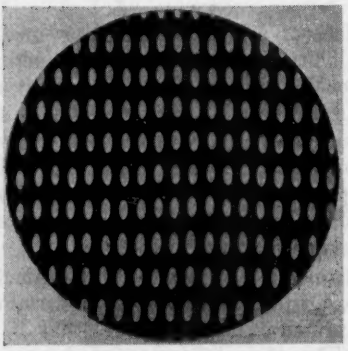
As Multipore is a relatively new development, the full extent of its application is yet to be realized. Its present use in two important fields and its possible application in another are discussed.



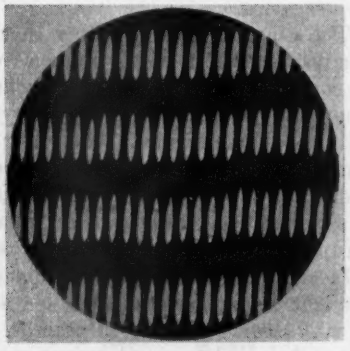
3200 holes/sq. in. plain Multipore pore diameter .005"-.006".



1100 holes/sq. in. plain Multipore pore diameter .015".



3200 hole Multipore expanded 50% in one direction.



3200 hole hard rubber Multipore expanded 250% in one direction.

FIG. 4.—Microphotographs of types of Multipore (7½ magnifications).

TABLE I

No. holes per sq. in.	Ave. hole diameter (inch)	Calculated % voids	Standard available thicknesses * (inch)	Max. width of sheet † (inches)	Max. length of sheet † (yards)
6,400	.004-.005	8-10	.030	42	38
3,200	.005-.006	6-7	.030, .050 .070, .090	42	38
1,700	.005-.007	5-6	.030, .050 .070, .090	42	38
1,100	.010-.012	10.13	.030, .050 .070, .090	42	38

* Other thicknesses can be produced to specification.
† Finished sheets can be joined.

Wearing Apparel

Plain soft rubber Multipore has been used for several years as a basis of a high-quality rubber bathing suit that will not hold water, has excellent tear resistance and is cool to wear. A nationally known corset manufacturer is now marketing a line of women's girdles and foundation garments made of Multipore. Soft rubber Multipore with 1,700 holes per square inch is usually used in both of these applications. Multipore has met with success in the clothing field, not only because of its unique porous characteristics, but because of the use of specially purified latex rubber.

Batteries

Expanded hard rubber Multipore has been used commercially in large quantities as a paste retainer in high-quality heavy-duty storage batteries, permitting construction of high capacity batteries with exceptionally long service life. These batteries are used in industrial trucks, air conditioning apparatus and train lighting systems.

Filtration

The use of a porous rubber sheeting in place of other types of filter media is advantageous in many processes where flexibility and resistance to the action of corrosive substances are important. However, prior to the development of Multipore no porous rubber or synthetic rubber sheeting was available with suitable characteristics. There are a number of specific applications in the filtration industry where Multipore looks promising. These include save-alls and other apparatus for the filtration of pulp in the paper industry; filtration of sewage sludge; mining ores; filtration of milk products; clarification of sugar, syrups, fruit juices, beer and corrosive liquids in the chemical industry.

In view of the fact that the smallest pore diameter in Multipore is 0.004-inch, it might be assumed that Multipore would be satisfactory only for the filtration of very coarse particle substances. It is a practical fact, however, that if a suspension or slurry contains some coarse particles, these bridge across the pores and retain the fines. This is illustrated by the data shown in Figure 5 for the filtration of a finely ground ore, all of which passed through a 100 mesh, and 86% of which passed through a 200-mesh sieve.

Direct Filtration of Granular Materials.—Experimental work has shown that Multipore may be used as a filtering medium for materials of a generally granular nature. Data on crushed ore samples typical of those filtered in the mining industry (Figure 5) show that if the proper type of Multipore is used, it has the following advantages over conventional filter cloths.

1. The smooth surface of Multipore and the absence of surface fibers permit the removal of much thinner cakes from the filter surface, thus increasing the capacity of a filter unit of the continuous type, such as the Oliver or Dorrco rotary filter.

2. Multipore apparently does not show progressive blinding. If any slight blinding should occur over a long period of time, Multipore can be cleaned either by flushing with water and air or by the application of chemicals, without injury to the rubber.

3. Multipore can be used over a wide range of temperatures for filtration of materials from corrosive solutions.

Against these advantages Multipore yields slightly higher solids in the filtrate during the first portion of the filtration cycle. However, for numerous processes in the mining and chemical industry it appears that this slightly turbid filtrate can either be recirculated or can be fed to an auxiliary "tailings" filter, using a conventional cloth depending on the type of material being filtered.

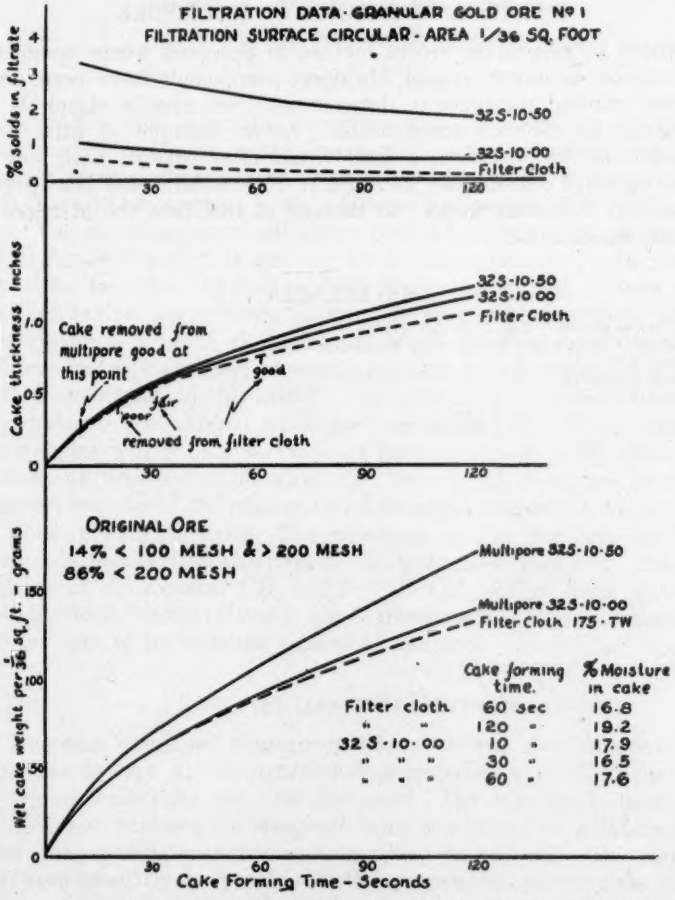

FILTRATION DATA · GRANULAR GOLD ORE Nº 1
FILTRATION SURFACE CIRCULAR · AREA 1/36 SQ. FOOT
% solids in filtrate
325-10-50
325-10-00
Filter Cloth
Cake thickness Inches
Cake removed from multipore good at this point
good
fair
poor
removed from filter cloth
ORIGINAL ORE
14% < 100 MESH & > 200 MESH
86% < 200 MESH
Multipore 325-10-50
Multipore 325-10-00
Filter Cloth 175 · TW
Wet cake weight per 1/36 sq. ft. - grams
Cake forming time.
% Moisture in cake
Filter cloth 60 sec 16.8
" " 120 " 19.2
325-10-00 10 " 17.9
" " " 30 " 16.5
" " " 60 " 17.6
Cake Forming Time - Seconds

FIG. 5.—Multipore vs. filter cloth as filter media for granular gold ore.

Clarification of Liquids.—The clarification of liquids is usually accomplished by the precoat method, which involves the use of a layer of finely divided diatomaceous earth (Celite, Filter Aid) on top of a porous backing. In the clarification of corrosive liquids, sugar syrups, fruit juices, etc., the principal problem is to find a porous material to hold the precoat, that will have a reasonably long life under the severe operating conditions. The various types of filter-aid such as Celite are retained by plain Multipore provided the pore diameter is less than 0.007-inch, and by expanded Multipore provided the minor axis of the elliptical opening is below this figure. It appears that Multipore

will be superior to other types of porous backings for many operations because of: (1) resistance to corrosion; (2) greater mechanical strength; (3) elasticity and long flexing life; (4) smooth surface—ease of cleaning; (5) cost, based on actual tonnage filtered; (6) absence of thermoplastic effects at high temperatures in most types.

CHEMICAL RESISTANCE OF MULTIPORE

In addition to all-purpose stocks for use in processes where operating conditions are not so severe, special Multipore compounds have been developed that exhibit unusual resistance to deterioration from specific chemicals in high concentrations at elevated temperatures. As an example of what has been accomplished in this direction, a large drum filter covered with soft rubber Multipore operated continuously in a bath of 25% sulfuric acid at a temperature of 180 to 190° F. for six weeks. At the end of this time the Multipore cover was in perfect condition.

REFERENCES

[1] Goodyear, "Gum-Elastic", Vol. 1, p. 201 (1855).
[2] Product of the United States Rubber Co., Mechanical Division.
[3] *U. S. patent* 2,032,941.
[4] *U. S. patent* 2,032,942.
[5] *U. S. patent* 2,079,584.

PERMEABILITY OF NEOPRENE TO GASES *

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I. INTRODUCTION

The properties most generally associated with Neoprene are its rubber-like character and its resistance to the deteriorative action of mineral oils. To this combination of properties it owes its principal commercial applications. A less generally known characteristic is the relatively low permeability of this material to gases. The most suggestive ultilization of this property is in the construction of various forms of gas containers for use in lighter-than-air craft, particularly in view of the fact that the material may be readily applied to cloth as a continuous film having elastic extensibility. The work represented by this report was undertaken as a result of the interest which the Bureau of Aeronautics of the United States Navy Department maintains in all materials which offer promise of application in this field.

Since rubber is the material which has been employed to the greatest extent for gas containers, it is used as the basis for comparison in the present study. Aside from its practical application, the behavior of Neoprene toward gases is of interest because of the relation of its chemical composition to that of other dienes which possess elasticity. The substance used as the base for Neoprene compounds is polymerized chloroprene (2-chloro-1,3-butadiene). The chemical composition of chloroprene, $CH_2=CCl-CH=CH_2$ differs from that of other conjugated dienes, whose polymers are characterized by elastic extensibility, in that 40 per cent of its molecule consists of chlorine.

II. MATERIALS AND METHODS

The Neoprene employed throughout this work was that designated by the manufacturer as type *E*. The compounding materials were all of the type and quality recommended for use with Neoprene. The compounds were prepared in the customary manner, the Neoprene being masticated on a differential-speed mill, the compounding ingredients being added on the mill. The rubber compounds were similarly prepared. In the preparation of cements the thinly sheeted materials were dissolved in toluene, which was kept in continuous agitation. The cements were filtered through cloth and stored in tinned containers.

The coated fabrics were prepared by applying a plurality of thin coats to a balloon cloth by means of a small spreading machine equipped with a doctor blade. The cloth was a closely woven cotton fabric weighing 2.05 oz. per sq. yd., and having a thread count of 120 in both warp and filling directions. The unsupported films were prepared in the same manner except that the base was uncoated Cellophane from which the films, after being cured, could be readily stripped[1].

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 22, No. 1, pages 71-79, January 1939.

Curing in all cases was effected in dry heat. For Neoprene the conditions were a 1-hour rise to 257° F (125° C) followed by 2 hours at 257° to 266° F (125° to 130° C).

Permeability was determined by means of a gas interferometer of the Rayleigh type. The apparatus and conditions of test have been previously described[2]. Except where otherwise noted, all determinations were made under the following standard conditions. The film or fabric is maintained at a temperature of 25° C, with air at atmospheric pressure (760 mm. of mercury) on one side of the specimen and the gas whose rate of permeation is being measured at an excess pressure of 30 mm. of water on the other side. Permeability is expressed as liters per square meter per 24 hours determined under these standard conditions. The permeabilities in metric units may be converted to their corresponding values in cubic feet per square yard per 24 hours by multiplying the former by the factor 0.0295. Specific permeabilities are expressed as milliliters per square centimeter per centimeter thickness per minute.

III. PERMEABILITY OF UNSUPPORTED FILMS

1. Effect of Thickness

In the preparation of unsupported films the following compound was employed:

Compounding ingredient	Parts by weight
Neoprene E	100
Magnesium oxide	10
Rosin	5
Carbon black (P-33)	5
Phenyl-β-naphthylamine (Neozone D)	2
Zinc oxide	10

Table I

Permeabilities of Unsupported Films of Neoprene

Thickness of film (cm.)	Permeability at 25° C and 1 atm. (l. per sq. m. per 24 hrs.)			Specific permeability at 25° C and 1 atm. (cc. per sq. cm. per cm. per min. × 10^6)		
	Hydrogen	Helium	Carbon dioxide	Hydrogen	Helium	Carbon dioxide
0.010	6.3	4.1	12.1	4.3	2.8	8.4
.010	6.0	3.7	11.6	4.1	2.5	8.0
.016	3.7	2.5	—	4.1	2.7	—
.017	3.9	2.7	8.3	4.5	3.1	9.7
.022	2.7	—	—	4.1	—	—
.029	2.1	—	—	4.2	—	—
.035	1.8	1.1	3.6	4.3	2.6	8.7
.039	1.6	—	—	4.3	—	—
.068	0.9	0.6	2.0	4.2	2.8	9.4
Average	—	—	—	4.2	2.7	8.8

The permeabilities to hydrogen, helium and carbon dioxide obtained with different thicknesses of films are presented in Table I. The close agreement of the specific permeabilities, calculated from the permeabilities of films of

various thickness, indicates that the rate of permeation is inversely proportional to the thickness. This is shown in Figure 1, in which is presented the relationship of the gas impedance (reciprocal of permeability) to the thickness of film.

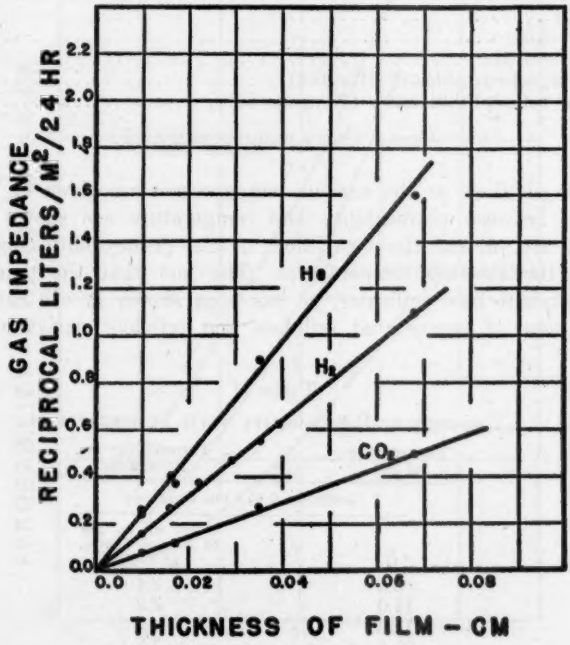

FIG. 1.—Relation of thickness of Neoprene films to gas impedance.

2. Relative Permeability to Gases

The average value of the ratio of helium permeability to hydrogen permeability of Neoprene, calculated from the values in Table I, is 0.65, which is the same as the corresponding value for rubber given in the literature. The average of the ratios for carbon dioxide to hydrogen is 2.0, which is somewhat lower than the corresponding values for rubber, which are reported as ranging from 2.46 to 2.91.

Values for the specific permeability of rubber to hydrogen, given in the literature, range from about 20×10^{-6} to 27×10^{-6} cc. per sq. cm. per min. for 1 cm. thickness. According to these values, it is apparent that the specific permeability of this Neoprene compound is about one-fifth to one-sixth that of rubber.

3. Effect of Temperature

For the determination of the effect of temperature on the permeability of Neoprene to hydrogen, the thickness of films chosen was such that convenient values for permeability could be obtained throughout a range of temperatures. For comparison, the permeability of a film of rubber was also measured under

the same conditions. The essential data concerning the rubber compound are as follows:

Compounding ingredient	Parts by weight
Smoked sheet rubber	100
Sulfur	4
Zinc oxide	5
Zinc stearate	1
Mercaptobenzothiazole (Captax)	1
Phenyl-β-naphthylamine (Neozone D)	1

Cure: Thirty minutes at 288° F.

The values obtained at the various temperatures are given in Table II, and the relations between permeability and temperature are shown in Figure 2. In Figure 3 are plotted the logarithms of the permeabilities against the reciprocals of the absolute temperatures. The fact that the points fall fairly closely on straight lines indicates, as has been shown in the case of rubber[3], and in the case of regenerated cellulose and cellulose derivatives[4], that the

TABLE II

VARIATION OF PERMEABILITY WITH TEMPERATURE

Temperature of test	Permeability to hydrogen
	Neoprene 0.014 cm thickness
°C	l. per sq. m. per 24 hrs. at 1 atm. at t° C
6.0	2.4
11.0	3.2
14.0	4.2
25.5	7.8
34.0	12.1
42.0	17.0
	Neoprene 0.014 cm thickness
7.0	1.5
15.2	2.5
24.7	4.3
34.0	6.7
43.0	9.6
	Rubber 0.031 cm thickness
6.0	4.8
10.0	5.5
16.4	7.3
24.0	10.6
34.0	15.1
42.0	20.3

increase in permeability with temperature is exponential. The dependence of permeability on temperature is expressed by means of the equation: $Q_m = Ae^{-E/(RT)}$, in which Q_m is the permeability at the temperature T in moles per square centimeters per second at 1 cm. thickness. A is a constant having the same dimensions as Q_m, which bears a relation to the spatial requirements of the reacting molecules. E is the activation energy expressed in calories per mole. R and T are the gas constant and absolute temperature, respectively. When

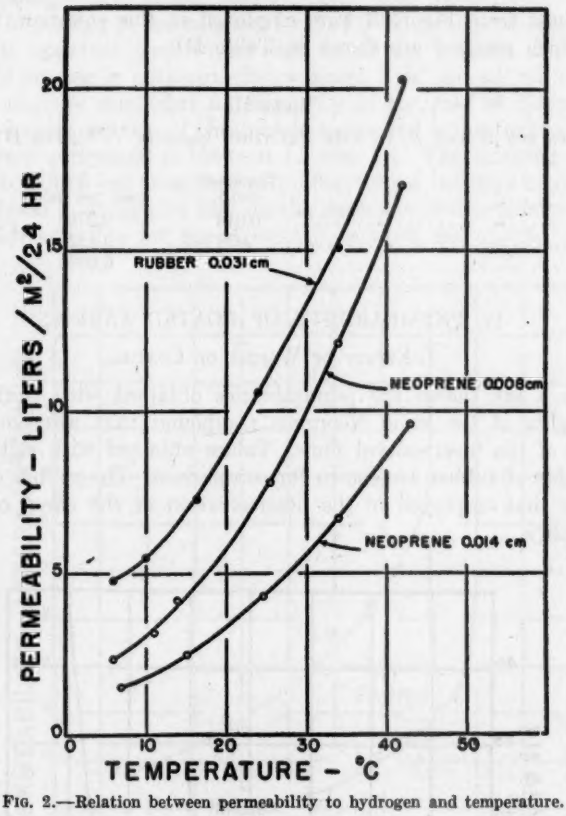

FIG. 2.—Relation between permeability to hydrogen and temperature.

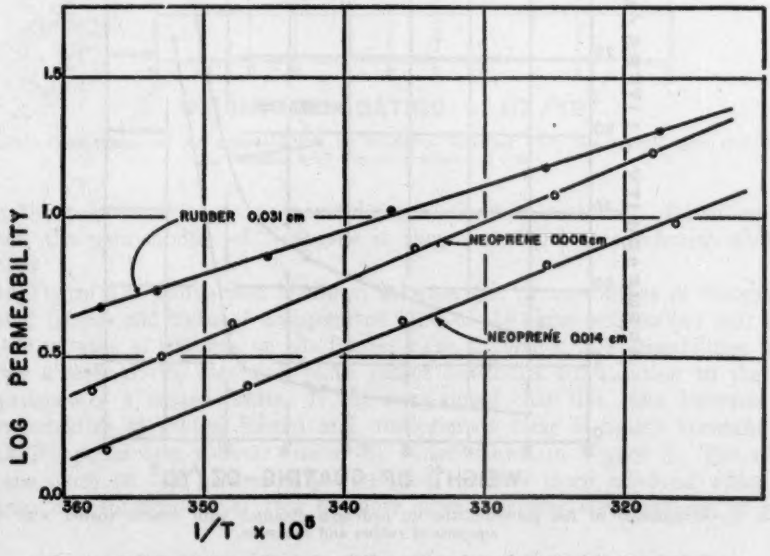

FIG. 3.—Relation between log permeability and reciprocal of absolute temperature.

values obtained from Figure 3 were employed in this equation, the values for E and A which resulted are shown in Table III.

TABLE III

VALUES FOR E AND A, IN THE EQUATION $Q_m = A_0 e^{-E/(RT)}$, FOR HYDROGEN

Material	Thickness (cm.)	E (cal. per mole)	A (Moles/cm.^{2} sec. for 1 cm. thickness)
Neoprene	0.014	9,376	22.2×10^{-6}
Neoprene	.008	9,422	24.2
Rubber	.031	6,998	2.2

IV. PERMEABILITY OF COATED FABRICS

1. EFFECT OF WEIGHT OF COATING

In Figure 4 are shown the permeabilities obtained with cloth coated with various weights of the same Neoprene compound that was employed in the preparation of the unsupported films. Values obtained with cloth coated with similar weights of rubber are shown for comparison. The rubber compound was the same as that employed in the determination of the effect of temperature on permeability.

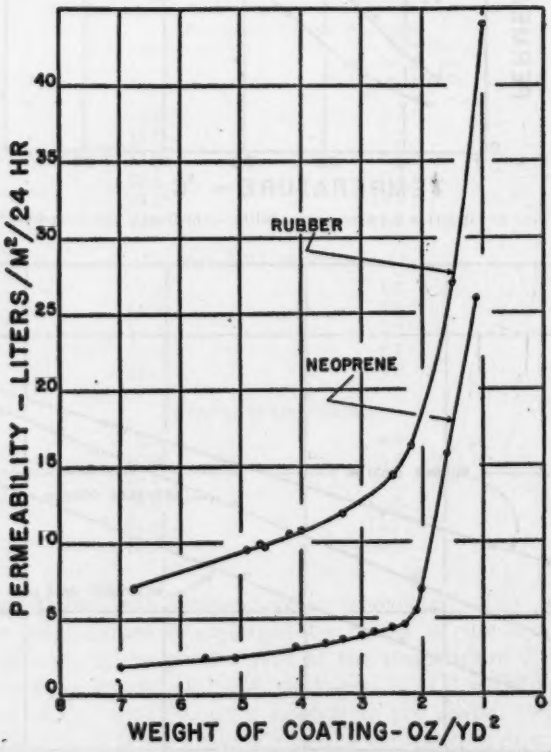

FIG. 4.—Comparison of the permeabilities to hydrogen obtained with fabrics coated with various amounts of rubber and Neoprene.

From the standpoint of airship-fabric construction, the permeabilities obtained with weights of coating in the neighborhood of 2 oz. per sq. yd. are of particular interest. It is apparent that within this range the greatest impedance for a unit weight of coating is obtained. Below about 2 oz. per sq. yd. of coating the permeability changes somewhat more rapidly in the case of Neoprene than of rubber. The specific gravity of the rubber compound is approximately 1.0; that of the Neoprene compound is between 1.3 and 1.4. The covering power of the latter is consequently less than that of rubber, and it becomes increasingly more difficult to obtain a continuous film on the cloth. It is this difference in specific gravities which accounts for the difference between the specific permeabilities

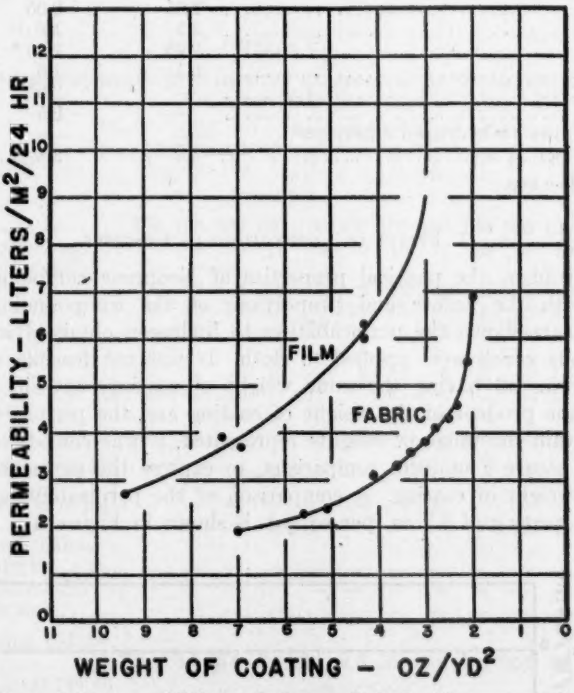

FIG. 5.—Comparison of the permeabilities to hydrogen obtained with unsupported film and fabric coated with the same weight of film.

and the permeabilities on a weight basis of the two materials. Based on the latter, the permeability of Neoprene is about one-third to one-fourth that of rubber.

In Figure 5 a comparison is shown between the permeabilities of Neoprene-coated fabrics and those of unsupported films of the same weights per unit area as the weights of coatings on the fabrics. The difference in permeabilities illustrates a well known fact that cloth makes a definite contribution to the gas impedance of a coated fabric. It has been noted that this ratio between the permeabilities of coated fabrics and unsupported films is nearly constant for both Neoprene and rubber within the range shown in Figure 5. The effect of the cloth on the permeability doubtless becomes more involved when the fabrics are constructed of two or more plies. Typical constructions of such

fabrics, employing Neoprene as coatings, and the permeabilities obtained are shown in Table IV.

TABLE IV

CHARACTERISTICS OF MULTIPLE-PLY FABRICS

Construction (order of layers in cross-section)	Type of fabric: Ballonet, oz. per sq. yd.	Airtight envelope, oz. per sq. yd.	Gastight envelope, oz. per sq. yd.
Aluminum-pigmented Neoprene	—	0.7	0.7
Neoprene	0.5	1.0	1.0
Cloth	2.05	2.05	2.05
Neoprene	3.5	1.6	1.6
Cloth	2.05	2.05 *	2.05 *
Neoprene	0.5	1.6	3.6
Cloth	—	2.05	2.05
Neoprene	—	0.5	0.5
Permeability to hydrogen (liters per sq. m. per 24 hrs.)	3.8	2.8	1.6

* Fabric laid on bias.

2. EFFECT OF COMPOSITION OF COATINGS

As with rubber, the physical properties of Neoprene compounds vary considerably with the nature and proportions of the compounding ingredients. In Table V are shown the permeabilities to hydrogen obtained with a number of compounds which were applied to cloth. It was not feasible to attempt to produce fabrics all having the same weight of coating, but since for a given compound the product of the weight of coating and the permeability is nearly constant within the range of weights represented, it was considered permissible, in order to secure a uniform comparison, to express the permeabilities relative to a single weight of coating. A comparison of the permeabilities calculated to a weight of coating of 3.5 oz. per sq. yd. is shown in Figure 6.

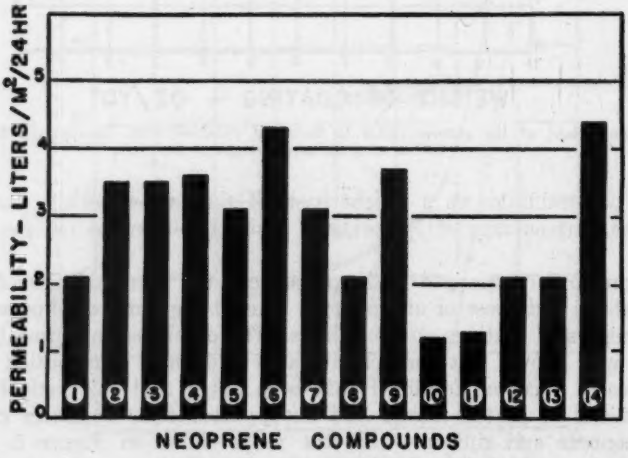

FIG. 6.—Comparison of the permeabilities obtained with the compounds given in Table 5 calculated to a uniform weight of coating of 3.5 oz. per sq. yd.

The compounds comprise two groups. Group 1 includes the conventional compounding materials which are added to secure satisfactory cure, increased flexibility, and similar characteristics. Group 2 contains, in addition, substances which are not usually associated with Neoprene.

The behavior of the compounds in the first group indicates that the inclusion of moderate amounts of the orthodox compounding ingredients does not appreciably affect the rate of permeation. This is in agreement with general experience in the behavior of rubber compounds. Of the compounds in the second group, the behavior of that containing spermaceti is noteworthy. It should be stated, however, that the relative permeabilities obtained with various compounds are not always reliable indications of their usefulness. Factors connected

TABLE V

EFFECT OF COMPOSITION OF NEOPRENE COMPOUNDS ON PERMEABILITIES OF COATED FABRICS

Ingredients	Compound (parts by weight)													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
GROUP 1														
Neoprene E	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Magnesium oxide	—	10	10	10	10	10	10	10	10	10	10	10	10	10
Phenyl-β-naphthylamine (Neozone D)	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Zinc oxide	—	10	10	10	10	10	10	10	10	10	10	10	10	10
Carbon black (P-33)	—	5	5	5	5	30	5	5	5	5	5	5	5	5
Sulfur	—	—	1	1	—	—	—	—	—	—	—	—	—	—
Wood rosin	—	—	—	10	—	5	5	5	5	5	5	—	5	5
Pine tar	—	—	—	—	10	—	—	—	—	—	—	—	—	—
Cottonseed oil	—	—	—	—	5	10	—	—	10	—	5	—	—	—
Cumar (P-25)	—	—	—	—	5	10	—	—	10	—	10	—	—	—
GROUP 2														
Paraffin wax (55° C m.p.)	—	—	—	—	—	—	5	20	—	—	—	—	—	—
Spermaceti	—	—	—	—	—	—	—	—	—	40	40	—	—	—
Chlorinated naphthalene resin (Arochlor)	—	—	—	—	—	—	—	—	—	—	—	40	—	—
Soft brown factice	—	—	—	—	—	—	—	—	40	—	—	—	—	—
Aluminum powder	—	—	—	—	—	—	—	—	—	—	—	—	40	80
Weight of coating (oz. per sq. yd.)	3.1	3.6	3.5	3.8	3.1	4.0	3.1	3.4	3.4	3.6	3.3	2.7	3.2	3.2
Permeability (liters per sq. m. per 24 hrs.)	2.4	3.4	3.5	3.4	3.5	3.8	3.6	2.2	3.9	1.2	1.4	2.8	2.3	4.9

with the manufacture, and the subsequent ability to withstand handling and exposure, of aircraft fabrics determine their utility to fully as great an extent as their rate of permeation. The behavior of the compounds containing aluminum powder is of interest since the presence of this pigment is of value because of its high reflecting power and opacity. The results obtained with paraffin illustrate the difficulty of employing a compounding material inherently incompatible with Neoprene. Paraffin wax itself is highly impermeable to hydrogen. Balloon cloth impregnated with about 2.4 oz. per sq. yd. of paraffin wax is permeable to hydrogen to the extent of only 0.5 liter per sq. m. per 24 hrs. Its use for aircraft fabrics is limited, for obvious reasons, to its supplementary employment on material such as rubberized fabric. An example of the treatment of a Neoprene-coated fabric in this manner is then of interest. The fabric coated with com-

pound 9 in Table IV was coated on one surface with 0.4 oz. per sq. yd. of paraffin wax (55° m. p.). The permeability to hydrogen of the fabric was reduced from 3.5 to 1.0 liters per sq. m. per 24 hrs.

3. Effect of Solvents Employed in Cements

Early in the experimental preparation of Neoprene-coated fabrics the formation of pinholes was a matter of considerable concern. Under the conditions of preparation the presence of these did not appear to be related to the nature of the compound nor to the number of coats applied. Furthermore, their persistence was not appreciably affected by the thickness of film built up on the fabric. The method of coating the fabrics was similar to that employed commercially except that the cements contained a higher percentage of solvent. The cement was applied to the cloth, which was under moderate tension, in several successive coats. A source of heat, in the form of heating coils, located

Table VI

Effect of Solvents in Cements on Pinhole Formation

	Evaporation at 140° F (60° C)		Evaporation at 78° F (25.5° C)	
Solvent	Weight of coating, oz. per sq. yd.	Permeability to hydrogen, liters per sq. m. per 24 hrs.	Weight of coating, oz. per sq. yd.	Permeability to hydrogen, liters per sq. m. per 24 hrs.
Carbon tetrachloride	3.1	>50	3.2	>50
Benzene	3.5	23	3.1	4.5
Toluene	3.6	3.1	2.8	4.6
Xylene	2.7	4.6	—	—

beneath the fabric hastened the evaporation of the solvent. It was considered advisable to compare films deposited from several different solvents which were suitable for Neoprene and economically within reason. Fabrics were coated with these cements under conditions of forced evaporation and at room temperature. The coated fabrics were examined, both before and after curing, over a light bank, for the presence of pinholes. No changes, so far as the presence of pinholes was concerned, occurred as the result of the curing. Excessive pinhole formation, as noted by visual inspection, corresponds to the high permeabilities in Table VI. Too rapid evaporation of the solvent may not always be the only cause of pinholes, but in extreme cases it would appear to be the most obvious contributing factor. Toluene or its equivalent is the most satisfactory solvent used.

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TESTING AND CONTROL OF LATEX SUPPLIES *

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INTRODUCTION

In recent years the employment of latex for a wide range of purposes has increased rapidly and the business of producing it in suitable forms on the market has become of considerable importance in the rubber-producing countries.

Consumers of latex have for some time realized the necessity of obtaining uniformity in their supplies—in many applications a much higher degree of uniformity is required for economical working than is called for in supplies of pale crepe or smoked sheet. In addition to the control of properties such as uniformity in rate of vulcanization, good aging, and absence of foreign matter, ordinarily required in supplies of the best grade of raw rubber, there are the problems of maintaining uniform concentration, stability, color, freedom from coagulum and absence of offensive odor. In some applications uniformity in the behavior of the latex under given conditions of compounding and coagulation is also required.

The general procedure observed in the collection, preservation and concentration of latex, together with a description of the various types of latex available, has already been given in the literature. It is proposed in this paper to review some of the tests that have been employed in evaluating and controlling latex supplies. An attempt will also be made to show the relative values of these tests in determining the suitability of latex supplies for different uses.

The procedure usually observed in assessing the quality of a consignment of latex is to determine the dry rubber content or percentage of total solids, alkalinity, amount of coagulum, and to report on the color, while sometimes the odor and the ability of the latex to withstand mechanical agitation are included.

An important step has recently been taken by the British Standards Institution in conjunction with representative bodies of the rubber industry in drawing up approved methods of carrying out the first four of these tests, which it is understood are shortly to be published; there is, therefore, no need to describe them in detail. The results of these tests would serve as a general buyers' guide for the purchase of latex consignments, but they may be open to misrepresentation. Cases arise, for instance, where an agreement is made to purchase latex on a dry rubber content. This presents no difficulty to the well-organized producer, providing that the degree of accuracy with which the dry rubber content (D.R.C.) can be determined is realized. This is governed by two main factors, namely, the difficulty of obtaining a representative sample of the consignment and the experimental error in carrying out the D.R.C. determination. It is now recognized that the D.R.C. decreases slightly during the first few months after the preparation of the latex, particularly in the case of unconcentrated latex. Although allowance is usually made for this by the producer, it

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may also be responsible for small differences between producer's and consumer's estimates of D.R.C.

The influence that these factors may have on D.R.C. determinations is shown in Tables I to III. Table I gives the results obtained by sampling in different ways drums of normal latex that had been stored for some months. The sampling tube used (Fig. 1) was designed to obtain a sample representative of the drum.

TABLE I

Method of sampling	Drum A % D.R.C.	Drum B % D.R.C.	Drum C % D.R.C.
(1) Sampling tube before disturbing the latex.	(38.0 to 38.1) 38.1	(38.78 to 38.73) 38.76	(38.95 to 38.85) 38.90
(2) Drum inverted for 2 hours, then sampled by sampling tube.	(37.4 to 37.2) 37.3	— —	(37.70 to 37.74) 37.72
(3) Drum rolled and rocked, then sampled by sampling tube.	(37.45 to 37.51) 37.48	— —	(37.40 to 37.42) 37.41
(4) Contents of drum emptied into an open drum, then thoroughly mixed by a plate stirrer and sampled without sampling tube.	(37.37 to 37.38) 37.38	(37.40 to 37.35) 37.40	(37.35 to 37.30) 37.33
Difference between (3) and (4).	0.10	—	0.08

TABLE II

Operator	D.R.C. %	Maximum difference
A	38.13	
	38.20	
B	38.10	
	38.22	
		0.19
C	38.10	
D	38.10	
E	38.29	

TABLE III

Drum	Estate laboratory, %	Laboratory A, %	Laboratory B, %	Laboratory C, %	Laboratory D, %	Maximum differences between A, B, C, & D, %
1	35.0	34.41	34.57(h)	34.2(l)	34.55	0.37
2	35.0	34.75	34.94(h)	34.74(l)	34.91	0.20
3	35.2	34.64(l)	34.9(h)	34.77	34.87	0.26
4	35.0	34.93	34.91	34.78(l)	35.04(h)	0.26

(h), (l): highest and lowest values among A—D

It is slowly lowered through the bung hole into the latex with the steel plug A in the open position, the air escaping through vents at the top. The tube is then sealed, removed from the drum, and the sample discharged. In spite of this elaboration, it will be noted that the samples drawn from the undisturbed drums are much higher in D.R.C. than those from the thoroughly mixed latices. On the other hand, the differences after the drums have been thoroughly rolled and rocked are of the order of 0.10%. The D.R.C. determinations were all carried out by the same person.

Table II gives the results of D.R.C. determinations made by five chemists on the same sample of latex in the same laboratory.

In Table III samples of latex were drawn from drums and submitted to four independent observers in different laboratories. Determinations made in Malaya after the drums had been freshly filled are included.

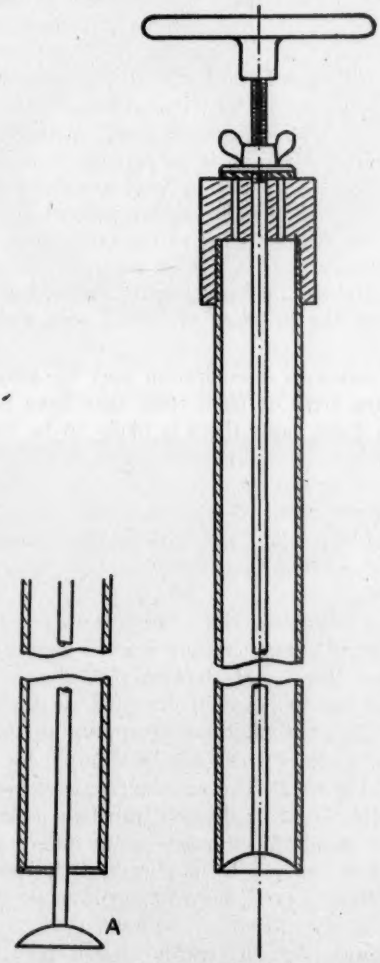

FIG. 1.—Latex sampling tube.

The conclusions to be drawn from these results are:

(*a*) That samples drawn by means of a sampling tube from drums that have been well rolled and rocked are substantially representative of the bulk.

(*b*) That the maximum difference to be expected in D.R.C. determinations made by different persons on samples that have been drawn in accordance with (*a*) is of the order of 0.3%, i.e., in an assessment of D.R.C. between producer and consumer it is reasonable to expect a tolerance of ±0.15%.

(*c*) That the time elapsing between the drawing of different samples for assessment purposes should be as short as possible.

COLOR OF LATEX

Of the four general tests mentioned above, the least well-defined is that of evaluating the color of latex. Normally this should be substantially white, but a grayish shade is not infrequent. The latter is due to the formation of iron sulfide from soluble sulfur compounds in the serum and iron—usually from iron containers[1]. Excessive grayness may denote delay in the addition of preservatives after tapping, with consequent partial putrefactive decomposition of the non-rubber components. For this reason it is sometimes associated with a putrefactive odor, which tends to persist in the dry rubber film. Other associated possible defects are reduction in stability and discoloration of the dry film.

Sometimes a yellowish color is encountered. Although this occurs less frequently than a gray discoloration, it is perhaps a more serious indication of abnormal quality. It can be caused by iron contamination in a well-preserved latex in which there is little reactive sulfur present, and is then often due to corrosion caused by electrolytic action at the boundaries of scaled and de-scaled areas of the iron container or at a welded seam, with the formation of colloidal iron hydroxide. Such corrosion may impart bad aging properties to the dry film, owing possibly to the presence of metals such as manganese and copper in the iron.

Another cause of yellowish discoloration may be associated with latex from first tappings of young trees or from trees that have been out of tapping for some time. While in these cases there is likely to be little inferiority in aging properties of the rubber film, abnormal behavior in coagulation and reduced stability may be experienced.

The existence of both types of contamination emphasizes the necessity for treating the insides of iron containers with an inert protective coating. A good grade of bitumen of medium hardness has been found satisfactory for the purpose.

A simple method of evaluating the color of latex has recently been developed by the London Advisory Committee for Rubber Research[2], in which the color is graded with respect to a chart showing nine shades of increasing grayness. This is undoubtedly a step in the right direction, as it enables an approximation of color to be made with the minimum of apparatus.

A somewhat similar method which has been in use for some time employs the color plate shown in Figure 2. The annular space surrounding the central cell, in which the sample is placed, is divided into two sections that are filled with inorganic cements of standard yellowish-cream and gray shades, respectively. The latex is enclosed in the cell by a plug and the plate then inverted. The sample is classed as Grade I or II according as its color is lighter or darker than those of the standards.

The shades that have been arbitrarily chosen for the standards have the following color compositions, expressed in Lovibond units:

	Blue	Red	Yellow
Gray	0.50	0.08	0.08
Yellowish-cream	—	0.10	0.40

The advantages of this method are that both sample and color shades are viewed through the same glass plate, both yellow and gray shades are classified, and the observer is not required to place the shade in one of several categories. If third and fourth classifications are necessary, a second color-plate can be used.

FIG. 2.—Latex color-grading plate.

FIG. 2A.—Filling latex color-grading plate.

COLOR OF DRY FILM

The value of supplementing the latex color-test by observing the color of the aged and unaged dry films has been described by Davey and Coker[3]. The use of such a test for choosing latex supplies for light-colored goods is obvious. The extent of discoloration of the heated film is of importance also when it is necessary to control the color of goods that are to be vulcanized by "dry heat." Samples of abnormally deep amber color may indicate iron contamination or latex from immature or freshly opened up tapping areas. Excessive darkening on heating may be associated with poor aging properties—particularly if the film exhibits undue tackiness. On the other hand, a latex that is moderately grayish in shade will often give aged and unaged films that would be classed as Grade I for color, *i.e.*, the samples would be unnecessarily declassed by the former test. This is illustrated in Table IV, in which the intensity of the color

Sample	Color of latex. Latex color grade	Color of film (Lovibond units)		
		Unaged	Heat aged for 16 hours at 94 to 96° C.	Film color grade
(*a*) Normal latex	Grade II	1.5	3.0	Grade I
(*b*) Normal latex	Grade I	3.0	9.4	Grade I
(*c*) Normal latex (from young trees)	Grade I	3.8	8.0	Grade II
(*d*) Normal latex (stored for some years)	Grade I	2.8	6.4	Grade I
(*e*) Normal latex (preserved with nonalkaline preservative)	Grade I	3.5	>26	Grade II
(*f*) Creamed concentrate	Grade II	1.5	3.5	Grade I
(*g*) Centrifuged 60% concentrate	Grade I	1.0	2.5	Grade I
(*h*) Twice-centrifuged 60% concentrate	Grade I	<1.0	1.3	Grade I
(*i*) Centrifuged latex from experimental area	Grade I	1.5	13.5	Grade II

of the dry film, measured by matching it with a series of standard Lovibond amber color glasses, is compared with the color grade of the latex. It will be noted that while samples *a* and *f* are Grade II for latex color, they yield films of comparatively low color intensities. On the other hand, with samples *c*, *e*, and *i*, the reverse happens.

For an accurate determination of film color a recognized type of tintometer such as the Lovibond or a photoelectric cell instrument is required, but for control work the device shown in Figure 3 has been found sufficient for the purpose. It consists of a holder with three apertures, through which is viewed white light reflected from the surface of a matt opal glass plate. The film to be examined is sandwiched between thin sheets of cellophane and 1-in. discs are punched from it, one of which is slipped into the central aperture. Standard amber color glasses are mounted in the other apertures. When creamed and centrifuged latices are to be tested, the color intensities of these glasses are 2.5 and 5.5 Lovibond units, respectively. For normal latex, color standards of 3 and 10 are employed. In each case the sample is classed as Grade I if the aged and unaged films are lighter in shade than the lighter and darker color standards, respectively.

In judging the color of films in this manner it is, of course, necessary to select discs of uniform thickness, and only those between 0.95 and 1.05 mm. in thickness, including that of the cellophane, are chosen.

For the heat-aging test, the film is heated in a boiling water oven at 94° to 96° C. for 16 hours before being placed between cellophane sheets. The method of preparing the films is described below.

FIG. 3.—Latex film color-testing apparatus.

STRENGTH OF AGED AND UNAGED FILMS

Another test which has been in use for some years in controlling supplies of 60% centrifuged latex is the determination of tensile strength of the heat-aged and unaged films. This can be conveniently carried out in conjunction with the film color tests as the same dry films may be employed. Davey and Coker[3] have recently described the use of such a test and have also summarized the experience of other workers in applying it to vulcanized films. Wohler[4] has stressed the influence of drying conditions on tensile strength figures, while Flint and Naunton[5], in describing their ingenious bubble bursting method, have shown the difficulty of obtaining consistent results from test-pieces of the order of 0.3 mm. in thickness. They also confirm the difficulty of obtaining satisfactory tensile readings from unvulcanized films.

It is, however, possible to obtain unvulcanized films thick enough to give readings of sufficient accuracy for control purposes. The aim has been, not so much to determine the tensile strength of the aged and unaged films with a high degree of accuracy, but to ensure that they do not give results below certain minimum values. If the latex has been so contaminated that it may yield finished products of poor strength or aging properties, the contamination is likely to cause appreciable lowering in the strength of the unvulcanized film. Pronounced film discoloration with low tensile strength in the heat-aged film is especially noted; the low tensile strength of aged films from latices adulterated with hydrogen peroxide has been shown by Davey and Coker[3].

A method of carrying out an "eliminating" test of this kind that has been found satisfactory is as follows:

Test-films are prepared by drying the latex in moulds 15.2 cm.×15.2 cm.×1.2 mm., which consist of glass plates held in wood frames by stainless steel flanges.

The frames are placed in a drying cupboard with four approximately level shelves arranged to take one row of four frames per shelf. The shelves are cut out for a length of about 2 in. at alternate ends and openings are provided at the top and bottom of the cupboard to allow a continuous draught, induced by placing a steam pipe below the bottom shelf through which is passed steam at a pressure of 5 lbs. per sq. in. The moulds in the three upper shelves are thus maintained at a temperature of 30° to 35° C. The lower shelf acts as a baffle for the warm air. Each frame is numbered according to its place on the shelves and carefully levelled by means of wood screws placed at its corners.

In the case of centrifuged or creamed concentrates, 40 cc. of the sample are poured evenly over the floor of the mould. After standing for a minute the surface is wiped slowly from side to side with a straight-edge to remove air bubbles. The mould is then placed in its position in the drying cupboard where it remains until the film is clear—usually in 16 hours.

A mould of depth 1.2 mm. will give a film, from 60% latex, approximately 0.8 mm. in thickness. In the case of normal latex, owing to the greater shrinkage on drying, cracks are apt to develop because of the adherence of the film to

TABLE V

TENSILE STRENGTH OF AGED AND UNAGED FILMS

Sample	Tensile strengths, kg. per sq. mm.	
	Unaged film	Aged film
Typical normal latex.....	(0.8, 1.2, 0.8, 0.8, 0.7) 0.9	(0.8, 0.7, 0.9, 0.8, 0.7) 0.8
Typical centrifuged 60% concentrate	(1.3 0.9, 1.1, 1.2, 1.3) 1.2	(0.7, 1.0, 0.8, 1.2, 0.7) 0.9
Normal latex (from a kerosene tin)	mean 0.4	mean 0.2
Normal latex preserved with a non-alkaline preservative ...	(0.3, 0.3, 0.1, 0.4, 0.3) 0.3	(0.1, 0.1, 0.2, 0.3, 0.3) 0.3

the edges of the mould. This can, however, be largely overcome by first painting the edges of the frame with molten ceresin wax, which reduces the adhesion. About the same thickness of film is obtained, as it is not necessary to wipe off the surface layer to remove air bubbles.

The dried films are removed from the plates by cutting with a razor blade along lines parallel with, and about a quarter of an inch from, the frame edges. The films are stripped, dusted with chalk, and placed in a water-oven for a few minutes to become flat at the edges. They are then tested for thickness in several places, the thickness being marked on each spot that is gauged. In this way a kind of contour map can be drawn on the surface from which areas of equal thickness may be selected for punching out test-pieces. Schopper rings are punched, using soap solution as a knife lubricant if necessary, and placed in a sulfuric acid desiccator for 48 hours in the case of films from centrifuged concentrate and 72 hours for normal latex films. They are then stretched at the rate of 30 in. per minute. For the heat-aging test the rings are heated for 16 hours at 94° to 96° C. before being placed in the desiccator.

Although Table V gives examples of results obtained on different aged and unaged samples, the test is used only as a limiting test, and samples are regarded as satisfactory if the averages of five readings from aged and unaged rings are not below 0.4 and 0.7 kg. per sq. mm., respectively.

STABILITY OF LATEX

It may now be of interest to review some tests that have been used in an attempt to evaluate the stability of latex. This is a problem that most users of latex have had to face in the purchase of supplies and control of their processes. The difficulty of devising a universal stability test capable of forecasting the behavior of all types of latex in their various uses is generally recognized. The best that can be expected of such a test is that it would give some assurance that the latex would withstand the normal conditions of shipment, storage and mechanical treatment without risk of coagulation. The rough test of rubbing latex in the palm of the hand is still the only one applied in many cases.

Probably the next most widely used is that in which the sample is subjected to violent agitation by means of a high-speed mixer, such as a Hamilton Beech Stirrer, the time required to produce partial or complete coagulation being taken as an index of stability. The sample is first adjusted to a D.R.C. of 30 to 34%,

TABLE VI

HIGH-SPEED STIRRING STABILITY TESTS—USE OF DIFFERENT END-POINTS

All samples adjusted to 34% D.R.C. and 0.5% NH_3

Speed of motor 14,000 revs. per min. Initial temperature 30° C.

Sample	Spotting on water, (minutes)	First appearance of clots, (minutes)	Large increase in current consumption, (minutes)
No. 1. Normal latex (average quality).	8 to 10	About 12	Indefinite
" 2. " "	5 to 6	4 to 5	About 7 (indefinite)
" 3. Normal latex (from young trees).	4 to 5	2 to 5	6 to 9
" 4. Centrifuged 60% latex.....	Indefinite	About 3	Indefinite
" 5. " " "	"	"	5 to 7
" 6. " " " (specially prepared)	"	4 to 7	9 to 13
" 7. Twice centrifuged 60% latex....	"	5 to 8	Indefinite (9 to 15)
" 8. 59% Creamed concentrate.....	8 to 9	7 to 8	10 to 12

then placed in a bottle of square section and subjected to the action of a small propeller rotating at 10,000 to 14,000 rev. per minute. The difficulty with this test is that of determining the end-point, which to a large extent is a matter of personal judgment. Different end-point observations have been used, such as noting the time for clots to appear, or observing the time required for a drop of the sample to coagulate on the surface of water. Jordan, Brass and Roe[6] take the rapid rise in current consumed by the motor as coagulation takes place.

Table VI gives results obtained on a number of latices, using these end-points. The latter can only be widely interpreted, as the samples differ considerably in their behavior towards coagulation: with some a fine curd or granular-like coagulation is formed some time before the presence of clots is detected, while in others more spontaneous clot formation takes place. The figures in Table VI imply, in fact, a degree of precision in determining the end-points that is not obtained.

Of the three end-points, probably the second, *i.e.*, the appearance of first clots, is the least unsatisfactory. The third end-point is often unreliable because of the tendency for a cylindrical compact clot to form round the stirrer, which rotates in the serum with little increase in the load on the motor. This has

happened in the case of samples 4 and 7. On the other hand, the first clot results of Nos. 2 and 6 suggest a greater similarity in stability than is indicated by the third end-point.

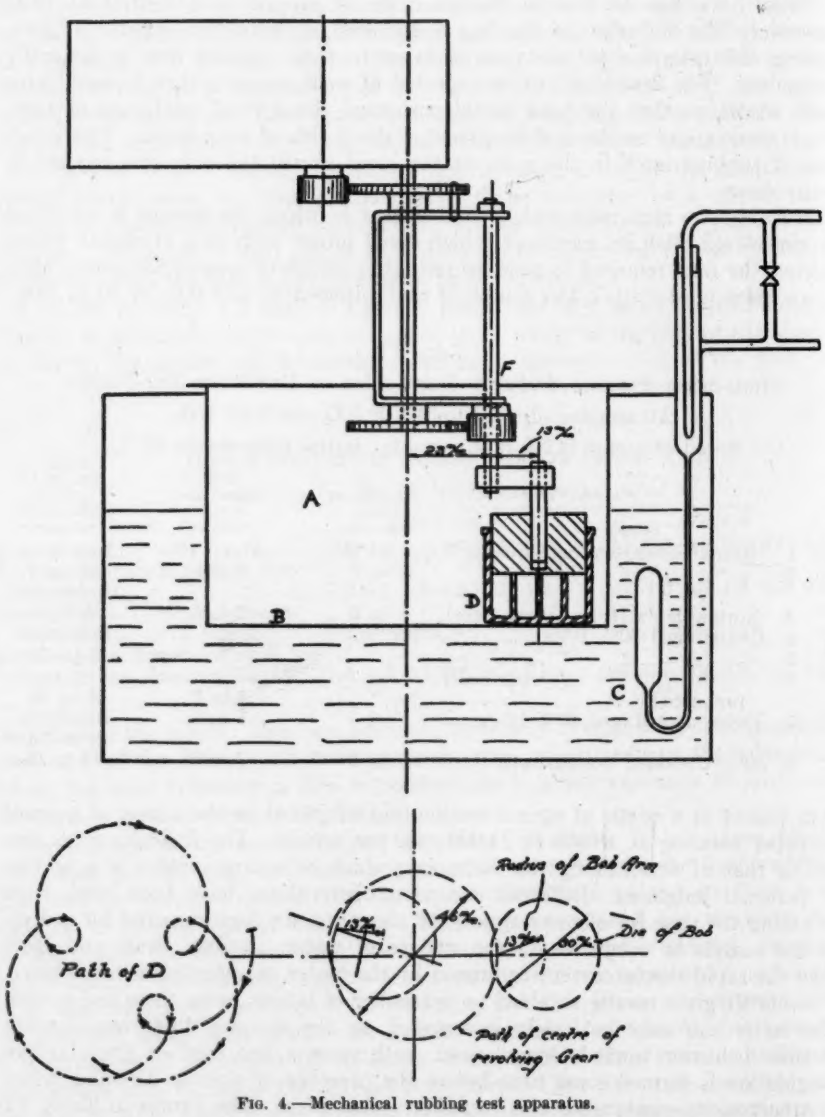

FIG. 4.—Mechanical rubbing test apparatus.

In an effort to obtain a more reliable mechanical stability test, an attempt has been made virtually to reproduce under controlled conditions the hand rubbing test in which coagulation is mainly brought about by the combined influences of friction and evaporation. The apparatus employed is shown diagrammatically in Figure 4. It consists of a container (A) with a glass base

(B) immersed in a constant-temperature water-bath (C) maintained at 45° C. A rubbing element (D), consisting of a moulded rubber nose rendered smooth by treatment with bromine—CCl_4 and adjusted to 100 g. in weight, rests freely on the glass surface. One cc. of the sample that has been adjusted to 34% D.R.C. and 0.5% NH_3 content is pipetted on to the plate and the rubbing element is then made to rotate with a sun-and-planet motion round the central axis (F) in such manner that it substantially rubs the whole of the surface in a non-repeating path. It travels 30 times per minute round the central axis and revolves on its own axis 78 times per minute. The humidity of the air in the vessel rapidly reaches equilibrium so that the rate of evaporation is approximately constant. The end-point is taken as the number of seconds for the

TABLE VII

Sample	A Hamilton Beech type high-speed stirring test 34% D.R.C. 0.5% NH_3	B Mechanical rubbing (M.R.T.) test 34% D.R.C. 0.5% NH_3 45° C.	C M.R.T. test +5% ZnO	D ZnO stirring test 34% D.R.C. 0.5% NH_3 50% ZnO 30° C.	E ZnO stirring test 34% D.R.C. 0.5% NH_3 5% ZnO 45° C.	F Z.O.T. test 34% D.R.C. 0.05% NH_3 20° C.	G Z.O.T. test 59% D.R.C. 0.05% NH_3 20° C.
1. Normal latex ...	About 12	120 to 130	100 to 109	About 1300	—	10	—
2. " " ...	4 to 5	128 to 133	85 to 86	115 to 120	—	13	Thick paste
3. Normal latex (from young trees)	3 to 5	126 to 137	81 to 88	330 to 365	—	60	—
4. Centrifuged 60% latex	About 3	124 to 127	80 to 85	48 to 50	110 to 120	—	117
5. Centrifuged 60% latex	"	135 to 145	45 to 45	18 to 25	60	7	>300
6. Centrifuged 60% latex (specially prepared)	4 to 7	150 to 160	117 to 118	60	305 to 320	—	22
7. Centrifuged 60% latex	4 to 6	115 to 118	81 to 82	55	225 to 240	—	200
8. Twice centrifuged 60% latex	5 to 8	169 to 173	120 to 122	43 to 45	205 to 210	—	19
9. Creamed 59% latex	8 to 9	140 to 149	118 to 119	560 to 565	545 to 675	—	56

film to commence to break up into small particles of coagulum, *i.e.*, when the first permanent clean glass trail behind the rubbing element is obtained.

Although the apparatus may appear somewhat intricate mechanically, the rubbing mechanism can be made sufficiently strong for experimental purposes from standard Meccano parts (excluding motor).

Table VII (column B) shows the type of result obtained, together with an indication of the repeatability of end-points. Here again the figures may be misleading as, in spite of the magnitude of the differences between maximum and minimum readings on some samples, the end-points are much more definite than those of the high-speed stirring test. It will be noted that there is rough agreement in the orders of stability given by the two tests except in the case of Sample No. 1, where the result given by the high-speed test is abnormally high owing to the granular nature of the coagulum obtained, which is avoided in the mechanical rubbing (M.R.T.) test.

This test is still in its infancy, and further work may indicate a better choice of constants to give greater discrimination in end-point. Sufficient has been done, however, to show that a test of this type is likely to be of greater value than the high-speed stirring test.

The stability tests described so far have been concerned with the ability of latex to withstand friction and evaporation, but it is frequently of importance to know something of its "chemical stability" *i.e.*, its behavior towards coagulating ions. Such tests would be of value in selecting latex for special purposes. For example, in some applications, as in the production of certain dipped goods, it is necessary that the latex shall be capable of coagulating rapidly to yield a firm coherent coagulum when a coagulant is applied. In others the feature of most importance is the ability of the latex to withstand the destabilizing action of compounding ingredients such as zinc oxide and water-soluble accelerators without the necessity of employing excessive amounts of stabilizers that may adversely affect the coagulating behavior of the compound or the properties of the finished goods.

In an attempt to determine the stability of latex towards compounding ingredients, stirring tests have been proposed in which the sample is first compounded with an active substance such as zinc oxide. Thus, the influence of zinc oxide on the high-speed stirring test is described by Noble[7]. A modification of this test has been employed by the London Advisory Committee for Rubber Research[2], 50 cc. of the sample, previously adjusted to a concentration of 30% D.R.C. and an alkalinity of 0.6% NH_3, are placed in a container maintained at 30° C. 50% of pure zinc oxide, based on the D.R.C., is added and the mixture is stirred at the rate of 600 to 2,000 rev. per min. by a vertically placed stirrer fitted with radial arms. The relative stability is measured by the number of revolutions required to cause coagulation, and the presence of zinc oxide gives a much sharper end-point than is obtained with the ordinary high-speed stirring test.

Results given by a substantially similar test applied to the samples described in Table VI are shown in Table VII (column D).

The apparatus employed in this case is shown in Figure 5.

Fifty cc. of the sample, adjusted to 34% D.R.C. and of 0.5% NH_3 content, were placed in the container (A), maintained at 30° C. by the thermostat bath (B). 8.5 g. of pure zinc oxide were introduced and the sample stirred at the rate of 1,250 rev. per min. by the stirrer (C). In this test the number of seconds for coagulation was taken as the end-point.

Although sharper and more defined end-points are obtained than with the ordinary high-speed stirring test, there is still a tendency for the end-points to be masked by the formation of loose flocculent or granular coagula. An example is shown by the high and indefinite end-points given by both the high-speed and zinc oxide stirring tests on Samples 1 and 9. A similar tendency, but in smaller extent, is also probably influencing the end-point given by Sample 3. In general, however, the presence of zinc oxide does show up greater differences between the samples than are indicated in columns A and B.

The much lower figures for the centrifuged samples cannot be taken as an indication of extreme instability towards zinc oxide in ordinary use, as the dilution from 60% to 34% and the absence of a large proportion of serum solids do not permit of direct comparison with the figures given by the unconcentrated latices. Owing to the relatively low serum solids, centrifuged concentrates do in fact give more sharply defined coagulation and stronger coagula in the

presence of zinc oxide than do normal latices—a feature of considerable value in many latex processes.

In columns E results are given for the stirring test as applied to the undiluted concentrates. In this case 5% of zinc oxide was added in the form of a 50% dispersion (using 4% gum acacia and 2% caustic potash as dispersing agents) and the sample allowed to stand one hour before testing. The temperature during the test was maintained at 45° C. The end point in E was more clearly defined than in D.

In order to determine the influence of zinc oxide on the mechanical rubbing test, experiments were made in which the sample had been allowed to stand for one hour in the presence of 5% of zinc oxide (added as the 50% dispersion)

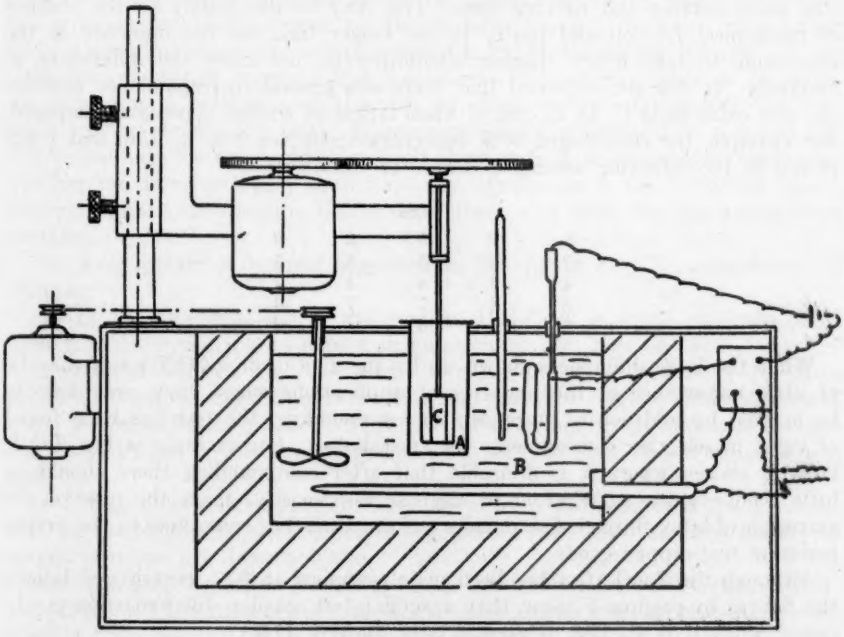

FIG. 5.—Zinc oxide stirring stability apparatus.

before the test was applied (Table VII, column C). It will be noted that although the zinc oxide has caused a general drop in the stability time and has given considerable improvement in the repeatability of the end-points, the relative agreement between the results and those of the zinc oxide stirring test is not very close. In the case of the normal latex samples this is probably again due to the suppression of the tendency to form flocculent coagula in the rubbing test.

Another test of the chemical stability type that has now been used for some time in the selection of centrifuged 60% latex for special purposes is the determination of the increase in viscosity of the sample in the presence of zinc oxide at low alkalinity and under carefully controlled conditions.

The sample is first adjusted to 59% D.R.C. and an alkalinity of 0.6% NH_3 and then neutralized to 0.05% NH_3. The latter operation is carried out by slowly spotting in the calculated amount of 38% formaldehyde solution with

vigorous stirring. Fifteen minutes after the addition, the alkalinity is determined by titration, using bromothymol blue as an indicator and further adjustment made if found necessary. 5% of zinc oxide, in the form of the 50% dispersion used in the previous tests, is stirred in and the sample allowed to stand at 20° C. for 24 hours. The viscosity is then determined by means of a simple jet type of instrument described by Twiss[8], and is expressed by the seconds required for 50 cc. to pass through a standard stainless steel aperture $\frac{1}{8}$-in. diameter and $\frac{1}{2}$ in. in length.

Results of this test when applied to the samples used for the other tests are given in Table VII (columns F and G). Here, however, the lower the figure the greater is the resistance to the action of zinc oxide. It will be noted that there is a greater differentiation between the samples than is shown by the zinc oxide stirring and rubbing tests. This may be due partly to the absence of mechanical friction and partly to the longer time for the influence of the zinc oxide to take effect. Higher alkalinities do not show the differences so markedly. It will also be noted that there is a general correspondence between the zinc oxide tests C, D, E, and G when latices of similar types are compared. For example, the centrifuged 60% concentrate samples Nos. 4, 5, 6, and 7 are placed in the following ascending orders of stability:

		Test		
B	C	D	E	G
7	5	5	5	5
4	7	4	4	7
5	4	7	7	4
6	6	6	6	6

While the large differences shown up by the zinc oxide (Z.O.T.) test may be of little importance in the majority of applications where they are likely to be masked by addition of stabilizers in compounding, the test has been found of value in selecting consignments for special uses. For example, a low Z.O.T. latex is chosen where it is desirable that after compounding there should be little tendency for aggregation or increase in viscosity, as in the case of the extrusion of latex through fine nozzles to form thread or sometimes in the preparation of fine dipped goods.

Although the Z.O.T. test has been mainly applied to 60% centrifuged latices, the figures in column F show that a similar but smaller differentiation is obtained when it is applied to normal latex at 34% D.R.C.

The effect of the presence of zinc oxide in the M.R.T. test is shown by comparing the second and third columns, B and C.

In an attempt to apply the Z.O.T. test to Sample 2 after it had been concentrated by evaporation to 59% D.R.C., a thick paste was obtained. This is representative of what normally happens and it is presumably due to the larger amount of active principle in the serum of the uncentrifuged latices. Conversely the Z.O.T. test of sample 5 when diluted to 34% D.R.C. was reduced from above 300 to 7.

The influence of the serum on zinc oxide activity is also indicated by the reduction in Z.O.T. that takes place on recentrifuging. Thus, the Z.O.T. value of Sample 7 was reduced from 200 to 19 after a second centrifuging (Sample 8).

Although it is not possible here to consider these results from a theoretical standpoint, it has been observed that among other factors the Z.O.T. value appears to be influenced by the extent of putrefactive degradation that has taken place in the serum, particularly when delay in preservation has occurred.

Sample No. 6, for example, was prepared under especially favorable conditions, while the ammonia contents, as received, of Samples 1 and 2 were 0.71% and 0.39%, respectively.

In reviewing the stability tests that have been described, the difficulty of applying such tests intelligently is realized. In the first place there is a risk of misinterpretation of results unless comparison is confined to samples of the same type, *e.g.*, normal latex, centrifuged latex, etc. Mechanical stability tests can give an approximate indication of general relative stability which should be sufficient for checking consignments to be used for general purposes. The results, however, should be widely interpreted, as the addition of even small proportions of stabilizers is likely to reduce considerably the differences indicated by such tests. There is evidence that a mechanical rubbing test of the type described could replace with advantage the high-speed stirring test, as it avoids the error in end-point caused by the variable manner in which coagulation takes place. For more precise applications a knowledge of the behavior of the latex towards active compounding ingredients such as zinc oxide is of value. An approximate indication of this can be obtained by carrying out the zinc oxide rubbing or stirring tests. Where considerable refinement is required the Z.O.T. test may be employed, but in all these tests it is desirable to determine whether the differences they show have any significance in the particular manufacturing process in question before using them as a basis for purchasing latex supplies.

The main points of interest suggested in this paper may be summarized as follows:

(1) In the determination of the average D.R.C. of a drum consignment of latex it is not reasonable to expect an accuracy greater than $\pm 0.15\%$.

(2) Simple methods for evaluating the colors of latices and their dry films suitable for commercial purposes are described and their relative values discussed.

(3) A method that has been employed for determining the strength of aged and unaged films is described, together with an indication of the value of this test.

(4) Methods of determining the stability of latex are compared and a substitute for the high-speed stirring test is suggested. Tests for evaluating latices for special purposes are described also.

In conclusion, the author wishes to thank the Dunlop Rubber Company, Ltd., and Dunlop Plantations, Ltd., in whose laboratories the experimental work described was carried out, for permission to publish this paper, also colleagues in these laboratories who have collaborated in the work.

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NOMENCLATURE OF SYNTHETIC RUBBERS *

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Sixty years ago, synthetic indigo, a dream of organic chemists, became a reality. Thirty years ago the increase in the knowledge of the chemistry of rubber made organic chemists dream also of synthesizing that important natural product. However, rubber or more specifically the rubber hydrocarbon has not yet been synthesized[8], in spite of the tremendous amount of time and effort already expended on this intriguing problem. But in scientific journals, books, newspapers and advertisements there is much that is published about "synthetic rubbers".

Indigo was synthesized, and there is no question about speaking of synthetic indigo. Since rubber has not been synthesized, why do we hear so much about synthetic rubbers? Are there any other names which could be used to describe the various "synthetic rubbers" and other rubberlike products? These are the questions which will be discussed in this paper.

Indigo is crystalline and can be purified easily; rubber hydrocarbon can be crystallized only under very special conditions, cannot be distilled, and therefore is not easy to purify. Indigo has a comparatively low molecular weight which can easily be determined; rubber hydrocarbon is an elastic polymer, the molecular weight of which is very high and cannot be determined with precision. A determination of the identity of natural and synthetic samples of indigo can readily be made, but with rubber it is almost impossible with our present methods to show the absolute identity of two specimens, although it is possible for all practical purposes to do so.

HISTORY OF SYNTHETIC RUBBER

As long ago as 1860 Williams[42] separated isoprene as a definite compound among the products of the destructive distillation of rubber. Fifteen years later Bouchardat[4] recognized the probable relation of isoprene to rubber and actually converted it to a rubberlike solid. In 1882 Tilden[38] discussed the possible industrial significance of the polymerizability of isoprene, provided it could be obtained commercially from a source other than natural rubber; in 1892 he reported[39] that isoprene which had been prepared from turpentine had spontaneously polymerized to a rubberlike product—he said "rubber."' Early in the present century Kondakoff[20] found that 2,3-dimethylbutadiene, a homolog of isoprene, slowly polymerizes to a rubberlike product, and similar observations were made concerning piperylene or 1-methylbutadiene[15, 37], and butadiene itself[14, 21].

Commercial quantities of "synthetic rubber" were manufatcured in Germany during the World War from 2,3-dimethylbutadiene; the product was known as methyl rubber[13, 30, 41].

There was a lull in synthetic rubber research until the rise in the price of rubber in 1925 furnished a stimulus to further work. In the present decade

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wonderful strides have been made, and now large quantities of "synthetic rubber" are being made from butadiene in Germany and Russia, and from a chloro derivative of butadiene (chloroprene) in this country. These "synthetic rubbers" are all prepared by processes of polymerization, and they bear a strong resemblance to natural rubber. They differ chemically from natural rubber, but most of them, especially the German Buna and the American Neoprene,

TABLE I

CLASSIFICATION FOR SYNTHETIC RUBBERS AND RUBBERLIKE PLASTICS

ELASTOMERS	Elastoprenes (derivatives of butadiene)	Butadiene rubbers Sodium-butadiene rubber, Russia [1, 13] Buna rubbers, Germany [19] Piperylene rubbers [15] Isoprene rubbers Polyprene: natural rubber Sodium-isoprene rubber [18] Heat-polymerized isoprene rubber [16] Dimethylbutadiene rubbers Cold polymer: methyl rubber H [13, 41] Heat polymer: methyl rubber W [13, 41] Haloprene rubbers Polychloroprene rubber: Neoprene [10] Polybromoprene rubber [9]
	Elastolenes	Polymers, such as polyisobutylene, formed in the presence of a catalyst, *e. g.*, boron trifluoride: Vistanex, Oppanol B [6, 21]
	Elastothiomers	Polyalkylene sulfides: Thiokol, Perduren [23, 27]
	Elastoplastics	Rubberlike polymers of acrylic and methacrylic esters: Acranal, Plexigum [29] Rubberlike mixed glyptals [42] Plasticized polyvinyl chloride: Koroseal, Igelite, Mipolam [7, 19] Polyvinyl acetate, above 40° C. [40] Polystyrene, above 65° C., and when partially solvated [24, 33, 40] Polyarylenethylenes or polyxylenes: AXF, from benzene, ethylene chloride and aluminum chloride [32] Polyphosphonitrilic chloride $(PNCl_2)_x$, an inorganic rubber [25, 29, 38]
PLASTOMERS	True thermoplastics	Shellac, polystyrene, polyvinyl acetate, celluloid, cellulose acetate
	Thermosetting plastics	Bakelite, glyptals, formaldehyde-urea polymers, acrylic resins

have physical properties which in the vulcanized state make them superior to similar products from natural rubber; *i.e.*, they are more resistant to the action of oils, fats, solvents, heat, air, sunlight and in some cases abrasion.

There are also other synthetic rubberlike materials, and some of them are called "synthetic rubbers," although they are not related chemically to natural rubber or to the polymeric derivatives of butadiene—namely, methyl methacrylate rubberlike polymers, polyalkylene sulfides (Thiokol), polyisobutylenes (Vis-

tanex, Oppanol), plasticized polyvinyl chloride (Koroseal), polystyrene above 65° C., polyvinyl acetate above 40° C., the inorganic rubberlike polyphosphonitrilic chloride, etc. They also must be classified.

All the synthetic substances so far mentioned have properties resembling rubber; they have been described in the literature not only as "synthetic rubbers" but also as "synthetic elastics," "rubberlike polymers," "rubberlike substances," "products with rubberlike properties," "plastic rubberlike materials," "rubbery polymers," etc. Rubber is also a plastic as well as an elastic substance and so are these other substances, but they all have these properties to different degrees.

THE TERM "SYNTHETIC RUBBER"

We can see, therefore, that the use of the term "synthetic rubber" has been widespread, although strictly speaking it is not properly used. However, when the situation is considered carefully, there does seem to be justification for it.

If a piece of "synthetic rubber" is handed to a man, he will note its similarity to natural or vulcanized rubber and quickly say, "That's rubber." If it is not natural or vulcanized rubber, then what should it be called? It may be called a substitute rubber or properly an artificial rubber.

Harries[15], who was one of the foremost workers in the field of synthetic rubber, wrote a book covering his researches, and he was careful at that time (1919) to use the German word *künstlichen* (artificial) rather than *synthetischen* (synthetic).

"Artificial" is a perfectly good word, but unfortunately it carries a connotation that is not always desirable. Artificial flowers, artificial light, artificial gems and artificial teeth illustrate this point. Artificial means "produced or modified by human skill or labor, in opposition to natural." The building up of an artificial rubber or a substitute for rubber is so much like a regular chemical synthesis of a desired product that the term "synthetic rubber" appears to be a good and appropriate name.

It is of interest that a somewhat similar situation has arisen in the nomenclature of artificial fibers. The name "rayon" was given to fibers and threads made from viscose to replace the term "artificial silk." At present there are several kinds of rayon made from different cellulose derivatives, and similar fibers are made from casein and resinous products; the latter are also sometimes called "rayon." In other words, rayon has become the name of a type of fiber. Similarly "synthetic rubber" covers a type of material.

Houwink[16] gave the following broad definition of a rubberlike material: "An organic material may be called a rubber when it shows a high elasticity of 100 per cent or more at room temperature, and when it does not lose this property upon storage at room temperature during considerable periods." This definition was criticized by Stevens[35], partly because it includes substances other than real rubber.

Midgley[24] discussed the question as follows:

It is impossible at the present time to define synthetic rubber in chemical terms. . . . . Expressed in physical terms, the simplest definition is, "those substances which possess the physical properties of rubber." Such a statement is functional, and should be revised in terms defining a unique physical property of rubber. Several organic substances of high molecular weight may be stretched to many times their original lengths, *i. e.*, gums, tars, waxes, jellies, etc.; but only rubber forcibly retracts to substantially its original size and shape after such

stretching. Hence the definition becomes: "Synthetic rubbers are those organic substances which possess the property of forcibly retracting to approximately their original size and shape after being greatly distorted, *i. e.*, such as being stretched x per cent of their original lengths." Here x is some arbitrary value. It should be over 100, probably 400, possibly 600, but certainly not higher.

Bridgwater[5] describes "synthetic substances with rubberlike properties" as substances that resemble rubber in the simple property of extensibility or deformability under moderate loads, coupled with a tendency to recover their original form when the load is removed, although not necessarily to a degree comparable to the recovery exhibited by natural rubber.

The question of the underlimit of extensibility and of the rate and extent of retraction of a substance to bring it into the class of synthetic rubber or rubberlike materials has never been settled. A decision by an international agreement of organizations interested in these materials and, in fact an international effort to bring order into the entire subject of rubber terminology, as already suggested by Dawson[11], would be helpful.

THE NAMES RUBBER, ISOPRENE, ETC.

Rubber was given its name because it has the property of rubbing out pencil marks, according to a record left by Joseph Priestley[2] in 1770; but the word was probably in use before that date. Languages other than English use words which were derived from the native words *caa o-chu* or *cahuchu*, meaning weeping tree—namely, *caoutchouc* in French, *Kautschuk* in German, etc. "Elastic gum" has been used in English, and similar words appear in Spanish and Italian, but rubber is not a true gum and therefore this is not a proper term.

The word "rubber" stands for more than a single chemical compound or a typical natural product. It is also used for vulcanized rubber and articles made from it—overshoes, elastic bands, etc. As Stevens[34] says, "It is not an elegant word, and its derivation is almost ludicrous in contrast with its modern applications." It is also not an international term. There is a question, therefore, whether it is advisable to use the word in a general term covering all types of rubberlike materials.

Weber named rubber hydrocarbon "polyprene," which was coined from polymer and isoprene. Isoprene was named by Williams[42] who states: "I have given the substance thus examined the name of *isoprene*. It would have been more grateful to me to have retained one of the names given by the previous observers, if that course had been possible; but Himly has not named the fluid discovered by him boiling between 33° and 44°, and the term *caoutchène* having been applied by Bouchardat to a fluid boiling at 14.5°, I could not adopt it; moreover, it is too like *caoutchine*." The suffix prene has also been used in chloroprene which is structurally similar to isoprene, with a chlorine atom in the place of the methyl group in position 2 of butadiene. Although the origin of the suffix prene is not known, it has been associated with rubber for many years and therefore is worth keeping in future names.

RECENT CLASS TERMS FOR RUBBERLIKE SUBSTANCES

Although there is some justification for the term "synthetic rubber," it seems best that it be used chiefly in connection with products that are related chemically to natural rubber—that is, to the various derivatives of butadiene. Usage, however, will determine this. At any rate there is a need for a single term which can be used to cover all rubberlike products.

TABLE II

STRUCTURAL NOTES ON THE SUBSTANCES ENUMERATED IN TABLE I

Starting Materials		Probable or Possible Structures of Polymers
Butadiene	$CH_2=CH-CH=CH_2$	$\text{——}CH_2-CH=CH-CH_2\text{——}CH_2-CH=CH-CH_2\text{——}$ The Russian synthetic rubber is a sodium-polymerized butadiene. The numbered Buna rubbers (Buna 32, etc.) are also sodium polymers. Buna S consists of mixed polymers of butadiene and styrene, polymerized in the form of an emulsion. Buna N similarly consists of mixed polymers of butadiene and acrylic nitrile ($CH_2=CH-CN$), prepared in the form of an emulsion.
Piperylene	$CH_3-CH=CH-CH=CH_2$	$\text{——}CH(CH_3)-CH=CH-CH_2\text{——}CH(CH_3)-CH=CH-CH_2\text{——}$
Isoprene	$CH_2=C(CH_3)-CH=CH_2$	$\text{——}CH_2-C(CH_3)=CH-CH_2\text{——}CH_2-C(CH_3)=CH-CH_2\text{——}$ In the natural rubber hydrocarbon, the methyl groups occur regularly along the chain. In the synthetic isoprene rubbers, the methyl groups occur more or less irregularly, since, when stretched, they do not give the x-ray fiber diagram. These unsymmetrical polymerides, judging from both chemical and x-ray results, have groupings somewhat as follows: $\text{——}CH_2-C(CH_3)=CH-CH_2\text{——}CH_2-C(CH_3)=CH-CH_2\text{——}CH_2-C(CH_3)=CH-CH_2\text{——}$
2,3-Dimethylbutadiene	$CH_2=C(CH_3)-C(CH_3)=CH_2$	$\text{——}CH_2-C(CH_3)=C(CH_3)-CH_2\text{——}CH_2-C(CH_3)=C(CH_3)-CH_2\text{——}$ The methyl groups occur regularly along the chain, as shown by chemical evidence, and this polymeric product when stretched gives an x-ray fiber diagram.
Chloroprene	$CH_2=C(Cl)-CH=CH_2$	$\text{——}CH_2-C(Cl)=CH-CH_2\text{——}CH_2-C(Cl)=CH-CH_2\text{——}$ In this polymeride the chlorine atoms evidently occur regularly, since when stretched it gives an x-ray fiber diagram.
Isobutylene	$CH_3-C(CH_3)=CH_2$ $\xrightarrow[-40°\ C.]{BF_3}$	Structure of the product is not known. The unsaturation is very low and probably occurs only in the "end molecule" of isobutylene. It is presumed that Oppanol B is the same or a similar substance. When stretched it gives an x-ray fiber diagram[6]
Ethylene chloride + sodium polysulfide	$CH_2Cl-CH_2Cl + NaS_x$	$HS-CH_2CH_2-S-S-CH_2CH_2\text{——}S-S-\ldots\ldots-CH_2CH_2-SH$ Similarly with 2,2′-dichloroethyl ether, $ClCH_2CH_2-O-CH_2CH_2Cl$, etc.
Methyl acrylate	$CH_2=CH-COOCH_3$	$\text{——}CH_2-CH(CH_2OCO)\text{——}CH_2-CH(CH_2OCO)\text{——}CH_2-CH(CH_2OCO)\text{——}$

TABLE II—CONTINUED

Table II—Continued

Methyl acrylate	$CH_2=CH-COOCH_3$	$\longrightarrow$ —$CH_2-CH(CH_3OCO)$—$CH_2-CH(CH_3OCO)$—$CH_2-CH(CH_3OCO)$—
Methyl methacrylate	$CH_2=C(CH_3)-COOCH_3$	$\longrightarrow$ —$CH_2-C(CH_3)(CH_3OCO)$—$CH_2-C(CH_3)(CH_3OCO)$—$CH_2-C(CH_3)(CH_3OCO)$—
Mixed glyptals	Phthalic anhydride + Glycerol + Ethylene glycol + Succinic anhydride	$\longrightarrow$ Mixed esters of high molecular weight
Vinyl chloride	$CH_2=CHCl$	$\longrightarrow$ —CH_2-CHCl—CH_2-CHCl—CH_2-CHCl—
Vinyl acetate	$CH_2=CH-OCOCH_3$	$\longrightarrow$ —$CH_2-CH(OCOCH_3)$—$CH_2-CH(OCOCH_3)$—$CH_2-CH(OCOCH_3)$—
Styrene (vinylbenzene)	$C_6H_5-CH=CH_2$	$\longrightarrow$ —$CH_2-CH(C_6H_5)$—$CH_2-CH(C_6H_5)$—$CH_2-CH(C_6H_5)$—$CH_2-CH(C_6H_5)$— This formulation is according to Staudinger[33]
		—$CH_2-CH(C_6H_5)$—$CH(C_6H_5)-CH_2$—$CH_2-CH(C_6H_5)$—$CH(C_6H_5)-CH_2$— This is according to Midgley *et al.*[25]
Ethylene chloride + benzene	$CH_2Cl-CH_2Cl + C_6H_6$	$\xrightarrow{AlCl_3}$ —$CH_2CH_2-C_6H_4$—$CH_2CH_2-C_6H_4$—$CH_2CH_2-C_6H_4$— The position of attachment on the benzene nucleus is not known; therefore, only the molecular formula is used.
Phosphorus pentachloride + ammonium chloride	$PCl_5 + NH_4Cl$	$\longrightarrow$ $(PNCl_2)_x$ —$P(Cl_2)=N$—$P(Cl_2)=N$— Phosphonitrilic chloride

The subject of the use of the words "synthetic rubber" and the need for a single term was discussed recently in the correspondence of Stevens[25], Barron[3], and Naunton[26]. In this correspondence the most desirable words suggested are "collastics," from colloid and elastic, by Barron, and the self-explanatory "elastoplasts" by Stevens, or "elastoplastics" as modified by Naunton. These have good derivations and are worthy of consideration.

Another suggestion is "caoutchoid" or "couchoid" by Patterson[28]. He points out that the word rubber is English and not an international word, and that therefore rubberoid (rubberlike) would not be generally acceptable. Accordingly he uses the word caoutchouc as the basis of a better derivative and suggests the words given. Since caoutchoid has "an abominable spelling" he thinks that the unpronounced letters could be dropped to form the simple term "couchoid."

These suggestions are good, and only time will tell how much they will be used. To the writer "collastic" seems to emphasize the colloidal property in preference to the more important elastic property of rubber. "Elastoplastic" has much to recommend it, although it has five syllables and is not easy to speak. "Couchoid" has an excellent derivation but it, too, is not easy to say.

NEW SUGGESTIONS

The writer also comes into the discussion with new suggestions, the first of which is "elastomer." This word is reminiscent of isomer, electromer, metamer and polymer, and it is hoped that it may prove of general service. In a conversation on this subject, the writer's colleague, W. C. Moore, suggested "plastomer" to cover the nonelastic plastic substances, and the writer presents elastomer to cover the elastic or rubberlike substances. Elastomer is easy to speak, has a scientific derivation, and emphasizes the elastic properties of all these substances.

For a general term to cover the rubberlike polymers of butadiene and its derivatives, including chloroprene, the writer suggests "elastoprenes"; for the polyisobutylenes, "elastolenes"; and for the polyethylene sulfides, "elastothiomers". The derivation of each of these terms is obvious. He further suggests that Stevens' term "elastoplastics" be used as the name of that growing class of rubberlike plastics which includes rubberlike glyptals and polymethyl methacrylates, plasticized vinyl chloride, etc.

CLASSIFICATION

Jacobs[17] recently classified synthetic rubbers under the following four headings: (1) halo- or halogenorubbers (Neoprene), (2) alternative or corubbers (Buna), (3) thiorubbers (Thiokol and Perduren), and (4) plasto- or resorubbers (vinyl polymers and other unvulcanizable thermoplastic polymers made from hydrocarbons)

The classification given in Table I is offered for all the synthetic rubbers and rubberlike polymers and plastics. Table II contains structural notes on the substances mentioned in Table I. The long bonds in the structural formulas of the polymers are used to indicate the places where the original molecules are joined together.

This article is not presumed to be the last word on the subject. It is written with the hope that it will help to clarify the present confused situation in regard to the use of the term "synthetic rubber," and to help classify all the substances with rubberlike properties. It is also hoped that the article will stimulate more thinking on the subject and soon bring order out of the present nomenclatural chaos.

After this paper was presented, the author accidentally came across the terms "lastic" and "synlastic," used by Ellis[12]. Also, his attention was called to the proposals of Kindscher[18], in which crude rubbers, synthetic rubbers (from butadiene and its derivatives, Thiokol, Neoprene, etc.) and rubberlike polyvinyl compounds, polyisobutylenes, etc., are classified under the terms *Kautschukgene, Kautschukoide,* and *Gummoide.*

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CONTRIBUTION TO THE HISTORY OF LATEX

LEO ECK

In RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 11, No. 3, pages 482-484, July 1938, is an article entitled "Contribution to the History of Latex" by Leo Eck. This article has since appeared in German in the *Gummi-Zeitung*, Vol. 53, No. 16, pages 421 and 423, with a bibliography which is not included in the original article.

This bibliography is therefore given here as a valuable adjunct to the original article in the earlier issue of RUBBER CHEMISTRY AND TECHNOLOGY.

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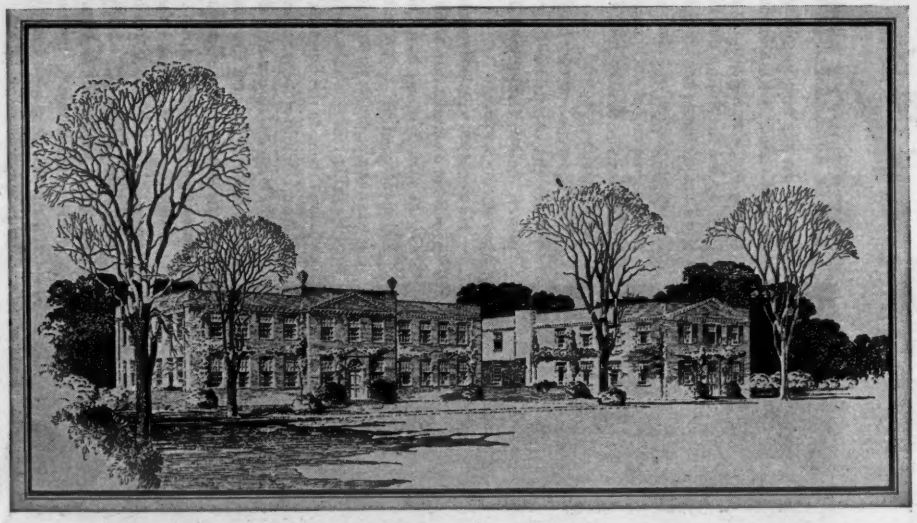

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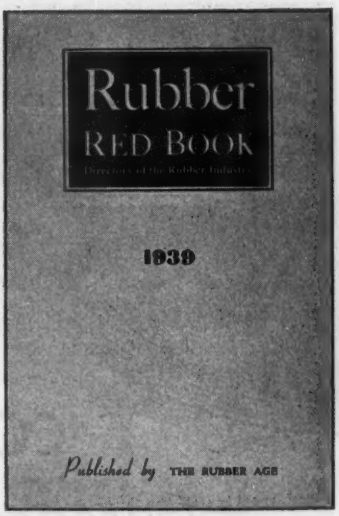

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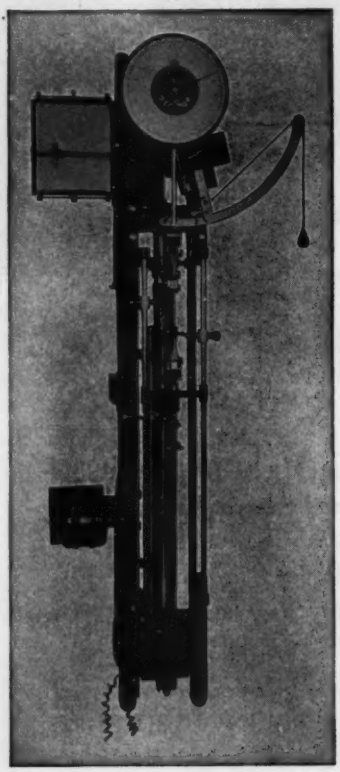

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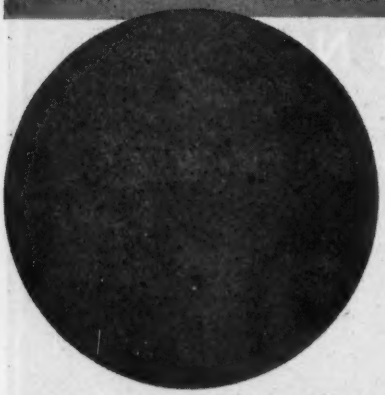
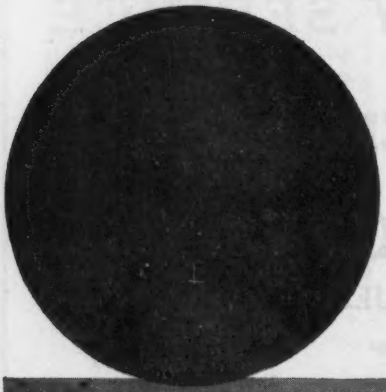


Photomicrograph of Dispersed Reclaimed Rubber

Photomicrograph of Normal Latex



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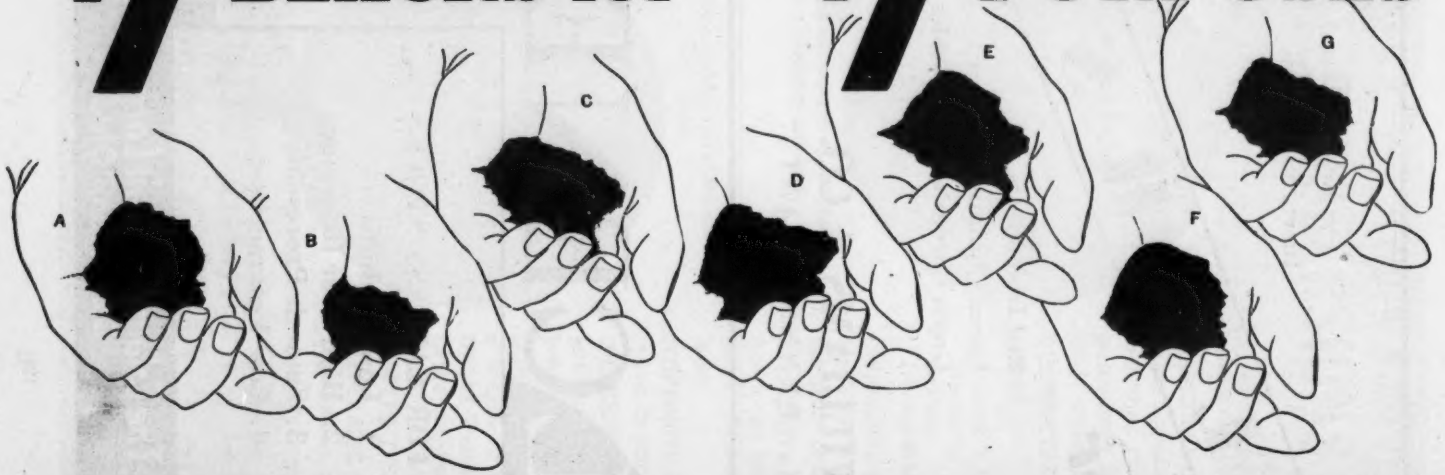

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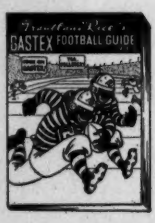

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